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Studies of the Fundamental Mechanisms of Contact Electrification

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Studies of the Fundamental Mechanisms of Contact Electrification

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of the requirements for the degree
Doctor of Philosophy in Physics

by

Rhyan Sheel Bose Ghosh

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ABSTRACT OF THE DISSERTATION

Studies of the Fundamental Mechanisms of Contact Electrification

by

Rhyan Sheel Bose Ghosh
Doctor of Philosophy in Physics
University of California, Los Angeles, 2022
Professor Seth J. Putterman, Chair

We present results of investigations into the underlying mechanisms that drive the long observed phenomenon of contact electrification. Our experiments indicate identical single-crystal insulators are able to exchange charge at magnitudes comparable to charge transfer between dissimilar materials. Any complete theory of contact electrification must be held accountable to these observations, leading to significant constraints on possible underlying mechanisms of charge transfer between insulators. This self-charging behavior does not appear random when repeated contacts are made, suggesting the possibility of a nucleation-type event developing from seed charges. The confirmation of such a mechanism would require a probe capable of monitoring the charge distribution on the materials' surfaces without affecting the charge distribution. This effect could be direct (e.g. via polar interactions between the tip and sample or by encouraging discharges to the probe) or requiring substantial time to collect data between charging contacts, which could allow for charge redistribution or neutralization, obscuring information on the growth of charge patches.

To this end, we demonstrate a novel non-destructive *in-situ* method of probing the charge distribution, including bipolar charging, on the surfaces of the contacting materials. This method also allows for determination of discharges and charge re-distribution during the experiment. This unprecedented understanding of charge carrier behavior immediately before and after contact provides key clues to the nature of the charge carriers in contact electrification and the underlying mechanism. These results provide constraints on both electron-dominant and ion-dominant theories of charge transfer and significantly narrows the field of possible mechanisms.

Another significant aspect of this work is that it provides an explanation as to why a subject studied with so much interest for such a substantial period of time has failed to provide a definitive understanding of the topic. We find charge transfer is highly variable, even in the situation of like materials, and provides insight as to why the results of contact electrification experiments can have such high variation between runs or even individual contacts. We have found that the nature of the contact between two insulating materials, in terms of alignment and amount of rub, have dramatic effects on the charging behavior.

The dissertation of Rhyan Sheel Bose Ghosh is approved.

Gary A. Williams

James Gimzewski

David Singh

Seth J. Putterman, Committee Chair

University of California, Los Angeles

2022

With particular thanks to Ana for her love and support over these many years, and without whom this would not have been possible…

and to my parents and my sibling for their love and support through this process

As someone who believes in a deterministic universe
I find life surprisingly unpredictable

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Author's Note: The work, summaries, and ideas presented here represents logical interpretations and conclusions based on the commonly accepted theories in chemistry and physics, but should not be construed as to imply the author's support of all of or as specific subset of those same theories. Further, within the commonly accepted theories we are working in the non-relativistic, non-cryogenic-temperature, non-ultrafast regime and the commonly accepted simplifications and approximations for working in such a regime are taken without further explicit statement.

CURRICULUM VITAE

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PUBLICATIONS

[1] R.S.B. Ghosh and J.E. Hirsch, “Spherical agglomeration of superconducting and normal microparticles with and without applied electric field,” Phys. Rev. **B86**, 054511 (2012), arXiv:1207.3773 [cond-mat.supr-con] .

CHAPTER 1

Introduction to Contact Electrification

Contact electrification, also referred to as triboelectrification, is a ubiquitous phenomenon in which a pair of originally neutral materials exchange charge. *This is not understood.*

It would be surprising if the majority of graduate students in any physics program in the world (to whom this thesis is generally directed) were not shocked at this lack of knowledge. Even if this only occurred once in a very specific controlled environment in some laboratory, the mere observation of charge moving in a way that cannot be explained should be alarming, especially when the electromagnetic force which determines the movement of charged species is believed to be so well understood. However, even reviews published during the time of writing explicitly state there is no consensus as to the underlying mechanism [1]. Hopefully this statement has already sparked the thought that this cannot be true and has sent any reader searching the literature for contradictory proof. Unfortunately, not only is it true that the underlying mechanism is not understood, but the phenomenon itself is not a rare isolated incident that has only occasionally been observed. Rather, its effects are so common that almost every reader will relate to the shock one feels when charge accumulated from contact electrification during everyday movements discharges to a doorknob or other object. Nor are the observations new, with some of the first discussions of electricity by Charles Francois De Cisternay Du in 1733 mentioning how even the name ”electric” comes from the greek word for amber in a reference to the ease in which amber can undergo contact electrification [2, 3]. As will be described in the review of current theories below, it will become clear that it is not even understood what the charge carriers in contact electrification are- electrons, ions, or bulk material. For a phenomenon that has been the subject of scientific scrutiny since at least the 1700’s, while still being actively studied in 2022 [4], and is so ubiquitous that nearly every adult will have experienced its effects to not be understood, especially with the added fact that this relates to the movement of charge which is governed by the electromagnetic force believed to be so well understood, begs for the development of a comprehensive theory to become a priority for the scientific community, and can hopefully stir the reader to dive into this field.

For those not intrigued by the lack of explanation behind such a fundamental scientific question, there is the fact that contact electrification is of great practical interest as well. Electrostatic charging has been used as an energy source for particle accelerators [5] (which can in turn be used as an x-ray source capable of taking radiological photos [6, 7]), in certain copying and printing technologies utilizing charging of toner particles [8], and for powder processing including in the pharmaceutical industry (at the same time the charging of powders has proven detrimental and at times dangerous)[9]. Contact electrification is the source of both atmospheric and volcanic lightning [10, 11], electric discharges from contact electrification are a danger to sensitive electronic equipment including microchips, and surging adoption of electric vehicles has renewed interest in solid-state batteries in which understanding any charge exchange at solid-solid interfaces is critical [12]. Thus, developing a complete theory of contact electrification is not only of scientific interest, but would enable the polarity and magnitude of charge transfer to be predicted, allowing for any desired enhancement or suppression of charging in a wide range of application.

In addition to the phenomenon being inherently interesting at a fundamental scientific level, having such wide-ranging applications, and being such a common occurrence, the topic is peculiar as there have been any advancements in first principle theories governing wide-ranging and highly significant aspects of solid materials while even a basic understanding of contact electrification remains elusive. These other advancements include theories of thermal conductivity [13], crystal structure [14], and the occurrence of superconductivity [15] among others, yet for contact electrification there is no agreed upon first principles theory of how initially neutral bodies develop a net charge upon contact. Despite the lack of an *ab-initio* theory there exists a broad spectrum of phenomenological ideas. This is perhaps one of the longest, if not the longest, standing unsolved mysteries of condensed matter physics.

For the discussions in this thesis, we will be defining contact electrification as charge transfer between two initially neutral insulating solids. Although there may be liquids or gas present at the interface, we are focused on interactions in which both solids must be present for the observed charge exchange to occur. This thesis has three key purposes. The first is to discuss an apparatus, that when combined with proper analytics and appropriately chosen computer simulations, can make detailed measurements of contact charging in well-controlled settings. The apparatus is capable of measuring the normal force between samples, as well as the net charge transferred from contacting and rubbing the samples in a controlled background pressure. Analysis of these measurements combined with computer simulations provides detailed information regarding the exact charge distribution on the surfaces, including any bipolar charge distributions that might occur. The significance of this apparatus in measuring the charge distribution is that it is an *in-situ* probe taking measurements due to the charge distribution across the entire surface before, during, and after contact, that does not interfere with charge exchange, as no part of the apparatus is close to the interacting region of the experiment. It is worth emphasizing the difference between the apparatus presented here and a probe such as an AFM (atomic force microscope) [16, 17, 18, 19] used as a KPFM (Kelvin probe force microscope) [20, 21]. By the nature of its design, a KPFM must get extremely close to the material surface, possibly encouraging discharges or charge exchange with the metallic probe tip. On top of requiring access to the surface which prevents any measurements from taking place during charge exchange or quickly afterwards, KPFM can require significant time to probe any substantial surface area. This, in turn, could result in measurements of some redistributed charge rather than probing the original charge distribution the underlying mechanism led to. Any charge measurements are also affected by discharges and the apparatus presented in this thesis is able to monitor those discharges as they happen, instead of only collecting data on the transferred charge after discharges have occurred (or even probes that might take some data before a discharge and some after, without being able to identify or control for such situations) which can cause confounding results.

The second key purpose of this thesis is to present data on charge transfer between identical single-crystals. Without any intentional asymmetry in the contact we observe charge transfer can occur between samples of the same material at magnitudes comparable with charge transfer between dissimilar materials. The use of smooth single-crystals is to control for the possibility that surface regions could vary significantly between the samples, such as with polymers, and thus be the cause of charge exchange. This critical observation is highly significant because it both presents a possible cause for quantitative discrepancies and lack of repeatability from one contact electrification experiment to the next, and it requires that any complete theory of contact electrification be capable of predicting such self-charging including which materials would exhibit the phenomenon more or less strongly and place limits on the magnitudes of such transfers.

The last key purpose of this thesis is to organize the wide-ranging published ideas on contact electrification in a manner which makes them accountable to experiment. Of particular emphasis is the theories need not only be consistent with the variety of previously reported experiments, but with our critical observation of single-crystal self-charging. We will hold the theories accountable to this observation.

1.1 Charge Exchange Between Samples of the Same Single-Crystal

A detailed description of our experiment and procedures is covered in chapter 7, but we offer a brief description here before highlighting our key findings. In short, in a vacuum chamber maintained at less than 10^{-3} Torr, two $1cm \times 1cm$ planar insulators comprised of single-crystals are brought into contact, a $1mm$ transverse rub is applied, and then the crystals are separated and the net charge on one crystal is measured. During this contact and separation the normal force between the crystals is measured. This procedure is repeated many times to observe the change in charging from one contact to the next. Each experiment for a pair of crystals consists of a set of several runs. Before each run the chamber is opened and the crystals are gently cleaned with isopropanol, which also neutralizes the net charge on the crystals. Each set is further divided into subsets of runs, where crystals are aligned by eye after cleaning before the first run of each subset, with no alignment occurring before the following runs of the subset. An example of our results for self-charging of identical crystals is displayed in Figure 1.1 discussed below. In our analysis of the experiment we attempt to interpret the data via various simulations of the electrostatic forces between charged surfaces using COMSOL.

An example of our results for self-charging are displayed in Figure 1.1. This particular example is highlighted for several reasons. The first is that within a single sub-set, where there is no realignment between runs, the three runs display dramatic changes in charging behavior. The first run of the subset charges positively (with regards to the crystal being measured, as the materials are the same), then after just three contacts starts to slowly discharge. The second run of the subset charges with a slightly larger magnitude, but with opposite polarity. Then in the final run of the subset, we obtain the largest magnitude of charge transfer, and it is worth noting that this occurs immediately after the largest charge transfer with opposite polarity, again without any realignment between the runs. The unique charging patterns demonstrate the difficulty in getting repeatable contact electrification results, even with two samples made of the same material, with no intentional asymmetry in the contact. In fact, these results help illuminate how it can be difficult to even get a *zero* net-charge transfer result. Using two single-crystals of the same material, with surface roughness Ra < 5 Å, is not enough to guarantee that little or no net-charge transfer will occur, let alone prevent bipolar transfer that could cancel out on macroscopic scales.

Figure 1.2 shows the detailed results of our self-charging experiments for the rest of the crystals, so that the large qualitative differences between crystals and within the experiments for a single pair of crystals can be seen. These same results are summarized in Figure 1.3 to give a better quantitative sense of how the variations from run to run statistically differ from one crystal pair to the next.

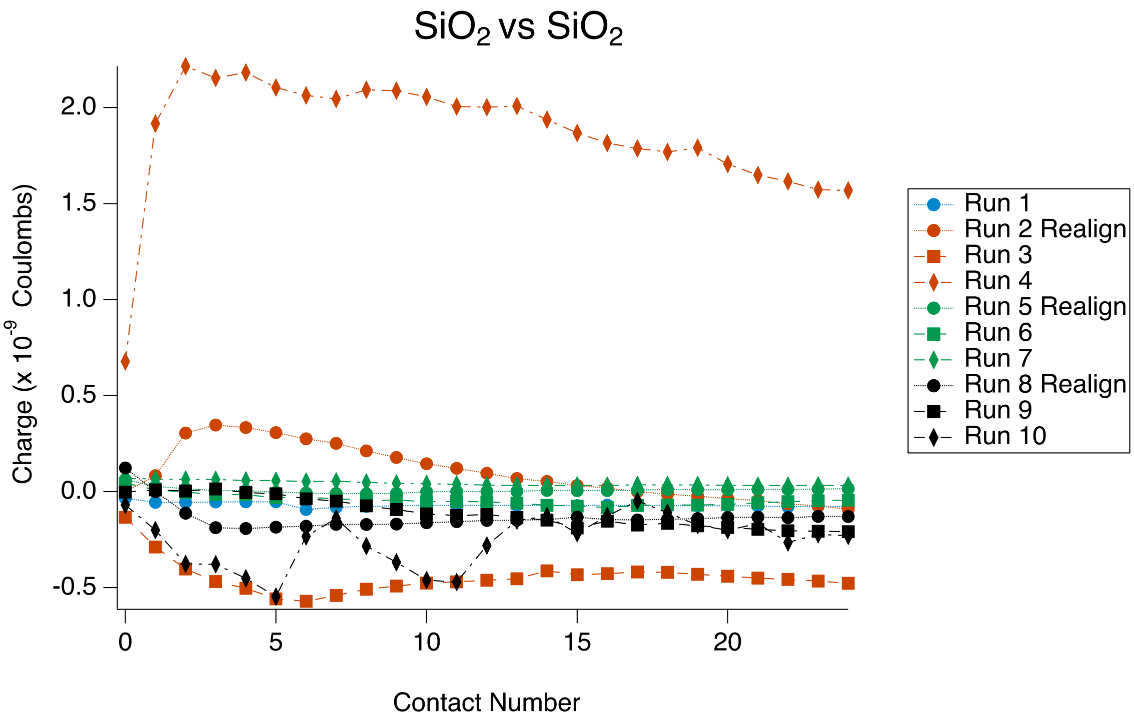

Figure 1.1: An example of raw charge data, in this case taken for two SiO_2 (0001) crystals contacted with ∼1.5 *N* of force and rubbed 1 *mm* back and forth. There are no realignments within a sub-set, each sub-set is displayed in a unique color. Notice the red sub-set contains the run with the largest magnitude of charge transfer as well as bipolar charging, indicating that the level of alignment within our control is not responsible for the dramatic qualitative differences in charging behavior.

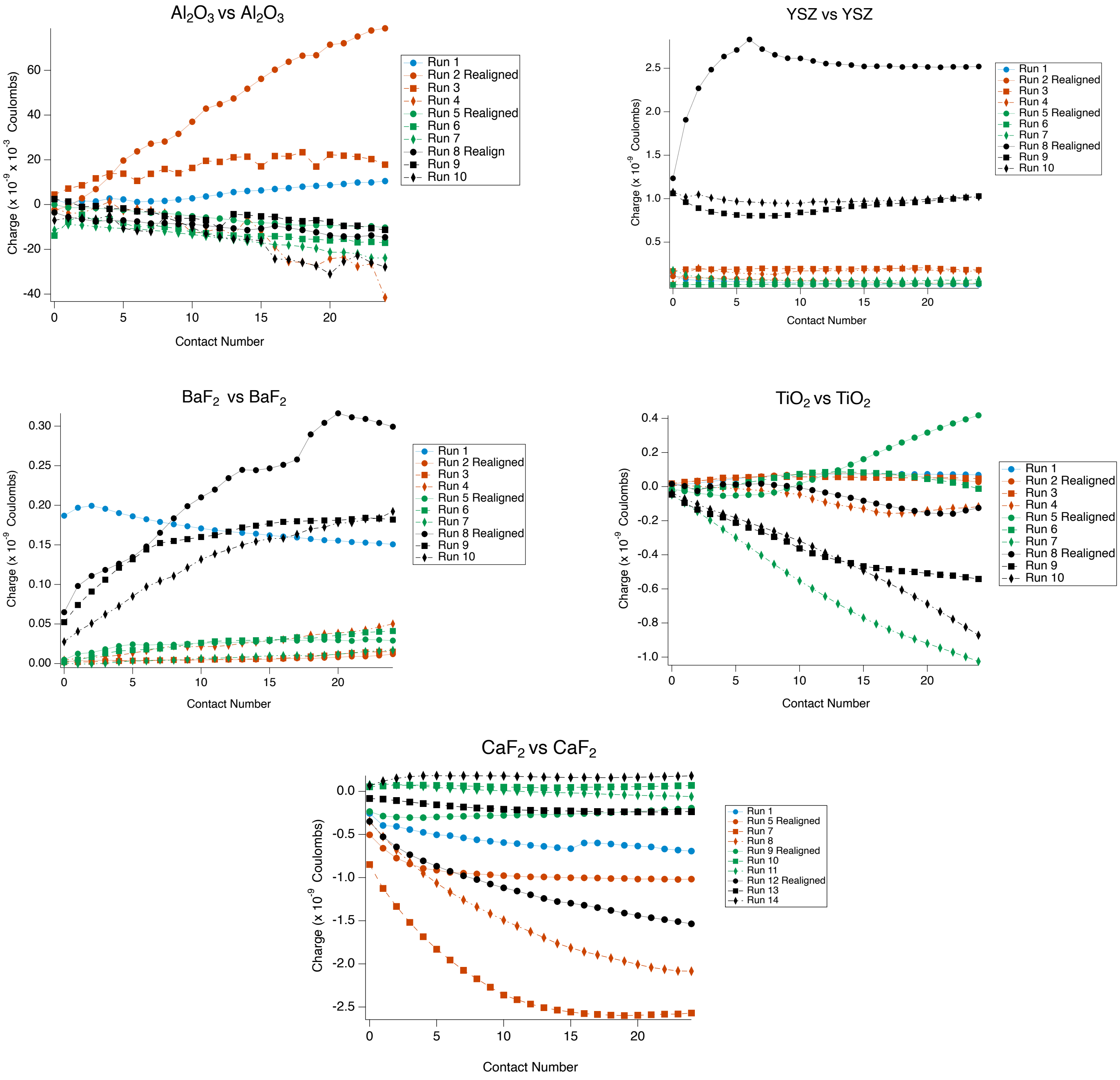

Figure 1.2: The results of contacting two samples of the same material for various crystal types. All follow the same procedure and are contacted with ∼1.5 N of force and rubbed 1 mm back and forth.

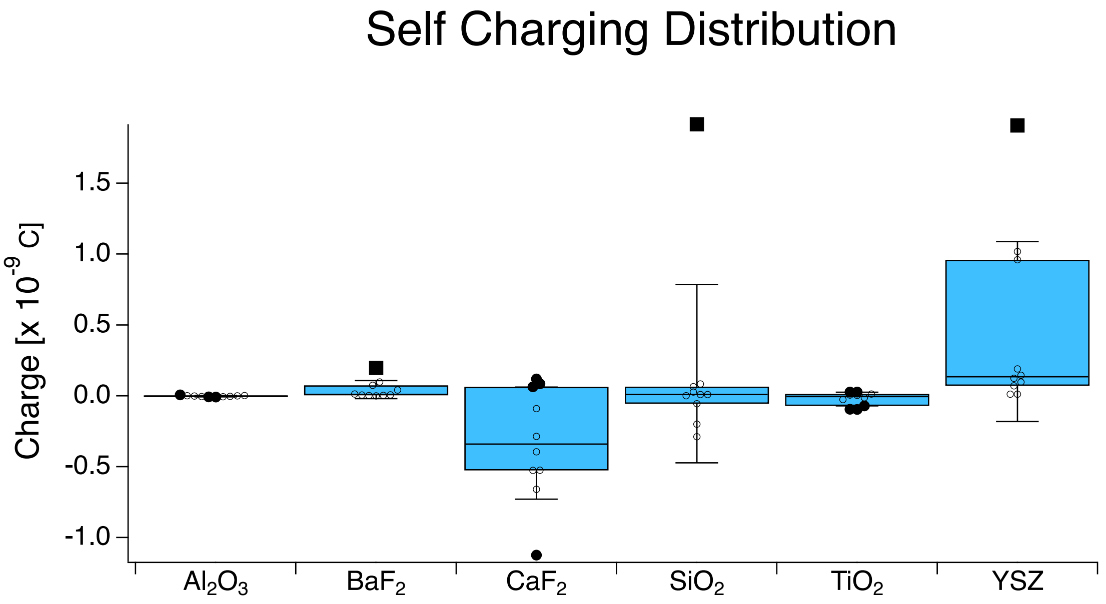

Figure 1.3: Distribution of total transferred charge after two contacts for the crystal pairs whose raw data is displayed in Figure 1.1 and Figure 1.2. Whiskers represent one standard deviation of the charge distribution, the line in the box is the median.

To better appreciate the significance of the self-charging results, we also present the charge distributions for the same set of crystals, when contacted against each other in Figure 1.4. Many pairs appear to exhibit the behavior of an expected ”triboelectric series” in the sense that for a given pair of crystals one type will tend to charge positively compared to the other (there is an exception for CaF_2 contacting YSZ). These results allow us to form a single-crystal triboelectric series, shown in Figure 1.5, free from the complications of working with polymers, polycrystals, or poorly defined materials used in previous studies [22, 23]. However, magnitude of transferred charge varies significantly from one run to the next, thus trying to incorporate a magnitude of charge transfer into the series becomes nearly impossible. The fact that the magnitude of charge transfer could vary from over $1nC$ to near zero for any of the crystal pairs is already enlightening as it provides a scale for how much charge transfer can vary even when conditions are being maintained as consistently as possible. This is fundamentally different from experiments with liquid-electrode reactions, for example, where the half-cell voltage is easy to reproduce. In reality, the data suggests a behavior even more radical than simply having wildly fluctuating charge transfer, which in the end could be due to some surface contamination or alignment issue. The data actually demonstrates that there can be polarity flips in the direction of net charge transfer for a given pair of crystals. For each crystal type in Figure 1.4 the self-charging results are included, which demonstrate that while the self-charging is often small compared to the net charge transfer between different crystal materials, there are clear examples (such as CaF_2 or YSZ) where the self-charging fluctuations are comparable to the largest fluctuations with dissimilar materials. Further, with SiO_2 or YSZ even the largest magnitude of self-charging is comparable to the largest net charge transfer when contacting other types of crystals.

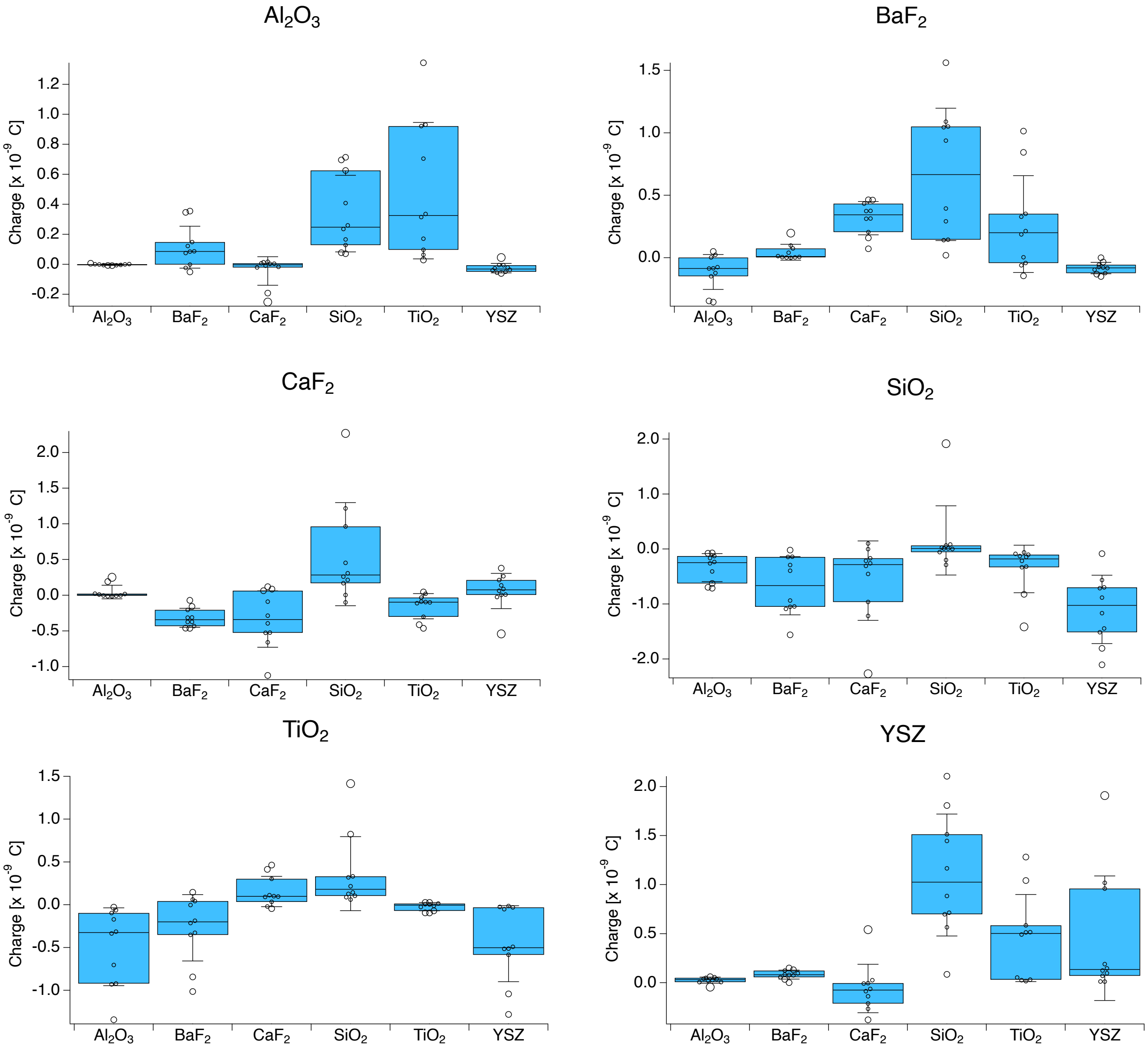

Figure 1.4: Distribution of total transferred charge after two contacts for pairs of dissimilar crystals. The sign of the charge corresponds to the sign of the net transfer to the crystal indicated in the title at the top of each graph. The circles represent individual data points to help illustrate the effect of outliers and to highlight the frequency of net polarity flipping between a given set of crystals.

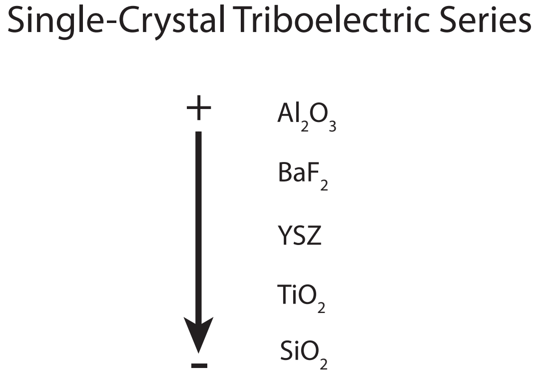

Figure 1.5: The resulting Triboelectric Series from our experiments between dissimilar single-crystal insulators. For our experiments, a given material acquired a net negative charge when contacted against materials above it in the series and gained a net positive charge when contacted against materials below it. CaF_2 is excluded from the series due to polarity flipping which leads to ambiguity in its placement

The importance of the self-charging observations goes beyond simply explaining why it would be difficult to obtain consistent results in terms of magnitude of charge transfer from one experiment to the next, which in turn makes it impossible to develop a quantitative theory of contact electrification. The actual importance is that any theory of contact electrification needs to explain this result. That is any *ab-initio* theory needs to address why two identical single-crystals would exchange charge, and whether this process is relevant for all contact electrification. If it is the same underlying mechanism for charge transfer between dissimilar materials, it could completely change which types of theories are applicable. Consider that in our self-charging experiments the polarity of charge can flip and the magnitude can vary substantially from one run to the next, but the polarity of charge transfer is consistent from one contact to the next such that any change is gradual. This is in contrast to a the behavior which would occur if the polarity is randomly assigned at any given point in the contacting region, in which the resulting transfer would mimicking the behavior of coin-flips. If the transfer has 50% probability of one polarity or the other, then for example the odds of having ten successive contacts with the same net charge transfer would be be just one in 512, yet we see such behavior repeatedly in our experiments. Instead, this would suggest some sort of charge equivalent of a nucleation event where once some initial charge has been transferred then continuing charge will tend to maintain the same polarity. This is both interesting because instead of charge transfer following a direction to neutralize the initial charge as normally would be expected, the charge flow goes to build up an increasing electric field and potential difference, and because the theory of contact electrification and explanation for a triboelectric series would completely change: now the first part would need to explain why certain pairs of materials would tend to create seed charge transfer always in a direction of a single polarity and the second part would describe how nucleation progresses.

It is valuable to compare the self-charging which we measure to the results published by the Grzybowski lab [24]. They studied charge transfer between pairs of $1cm \times 1cm$ samples made of the same polymer material and reported a mosaic pattern of positively and negatively charged domains. The domains have two characteristic length scales. The domains exist as larger ∼0.45 micron diameter patches, which themselves contain further fluctuations on a length scale of $44nm$. The authors calculate the potential above two oppositely charged patches close to this smaller length scale and show that it matches their measured potential above such a patch configuration reasonably well. From this they conclude the charge density in these regions is about 1 elementary charge per $10nm^2$, which is a local density of 10^{13} charges per cm^2 and a net charge of $\sim 2 \cdot 10^4$ charges per tile. The existence of the larger length scale suggests that while there might be small patches within a large patch, the small patches will tend to be mostly of one polarity, which is the only way to form the larger patch in the first place. Thus to get a sense of what net charge might be observed over the entire sample surface, we will assume tiles of ∼0.5 micron length, with a charge density of 1 elementary charge per $10nm^2$, where each tile is randomly assigned a polarity. This suggests $N_T = 4 \cdot 10^8$ tiles on a $1cm \times 1cm$ surface, each with a charge of about $q_T = 4 \cdot 10^{-15}$ C. For these values one gets a standard deviation of $\sigma_q = \frac{1}{2}\sqrt{N_T} \cdot q_T = 4 \cdot 10^{-11}$ C net charge. In terms of average charge density, this is ~ 0.05 nC/cm^2, only a factor of four from the authors' reported value, which we find to be reasonable for uncertainty in length scales and variations in patch sizes and charge density. For comparison, our samples are also $1cm \times 1cm$, but we observe average charge densities as high as $8.5 \cdot 10^{-1} nC/cm^2$ after a single contact between a pair of CaF_2 single-crystals, corresponding to a difference of 9 standard deviations if their mosaic picture applies to our crystals at the same scales. Thus, it is worth investigating if our materials exhibit larger patches of charge, resulting in the larger observed net charge density, or if there is some other mechanism involved.

To investigate the surface charging patterns on our crystals we developed a novel method of probing the charge distribution and average true charge density of our system using measurements of the normal force between crystals and COMSOL simulations.An example of such a force measurement is the black line in Figure 1.6. As a first approximation we follow the method of A.L. Collins and take the measured maximum normal force between the crystals just before contact to be given by $F = qE$, with q the actual measured charge, and the electric field of an infinite plane $E = \sigma/(2\epsilon_0)$, which immediately provides the estimated charge density $\sigma = F/q \cdot 2\epsilon_0$ [6]. In the case of single-polarity charge transfer, this further gives an estimate of the true area covered by this charge density as $A = q/\sigma$. Even assuming single-polarity charging, this method reliably provides a patch size significantly less than the size of the total sample surface. As an illustrative example, our analysis for the single contact self-charging of CaF_2 with a net charge transfer of $8.5 \cdot 10^{-1} nC/cm^2$ (see Figure 1.2), we calculate a charge density of $\sim 10 nC/cm^2$ implying a patch size of $\sim 8 \cdot 10^{-2} cm^2$ ($\sim 1.6 \cdot 10^{-3}$ m radius). Figure 1.6 shows a comparison of the force measurement as a function of crystal separation distance from our experiment with the COMSOL-simulated force for various single polarity patch sizes. This illustrates our new method's ability to provide information of the charge distribution with far greater detail. First, the largest force at smallest separation is shown to be due to a patch size between 1 and $2mm$. Particularly important is that the data for force as a function of separation can be seen to deviate from the force due to a single polarity patch. For increasing separation distance the physical data will always cross a calculated force curve when single polarity charging is assumed. Figure 1.7 illustrates how this type of behavior is characteristic of a surface with bipolar charging. One can see that the force curve for bipolar charging crosses the force curve for a single polarity patch of charge. This demonstrates that the charge distribution probe presented here is not only capable of providing information in single polarity charge distributions but can identify bipolar charging. The unique signature of bipolar charging enables the probe is able to provide information on all elements of the surface charge distribution, including patch sizes, charge per patch, distribution of patches, and any bipolar nature of the patches. We return to this in chapter 7. Instead of using a single data point to calculate the charge density, we are able to compare 10^3 data points to computer simulations with various charge distributions across the surface. The use of such a large set of data points allows for the possibility of identifying the exact charge distribution to the scale of interest, with only the exception of ambiguity from symmetry considerations that can be easily resolved in the future with strategically applied translation or rotation during crystal approach. We see that for our experiment with single-crystals, a single-polarity charge transfer would imply a patch size of radius just under $2 \cdot 10^{-3}\ m$ for $1\ nC$ net charge transfer.

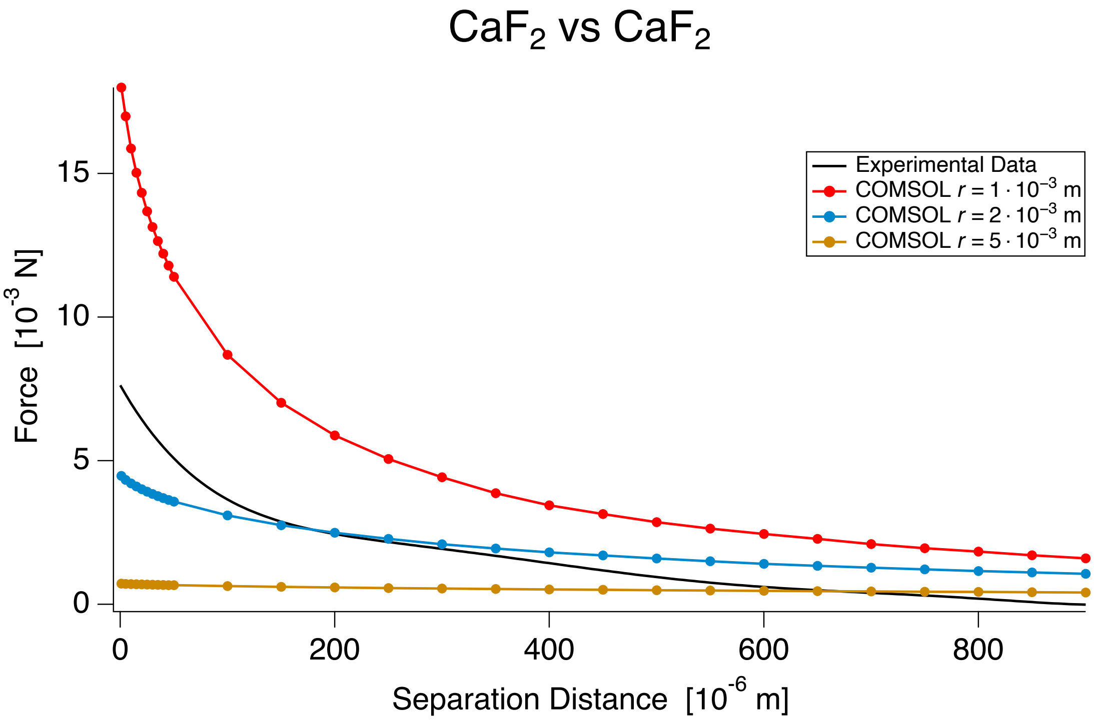

Figure 1.6: An example of COMSOL simulations of force versus separation distances between two equal and oppositely charged crystals with relative permittivity $\epsilon_r = 6.81$ (representing CaF_2) for various charge patch sizes, all with a net charge of $1nC$. The black line shows our actual data for CaF_2 self-charging, with a net charge of the same $1nC$. At small separation distances, the experimental data is bounded between the $1 \cdot 10^{-3}\ m$ and $2 \cdot 10^{-3}\ m$ simulations.

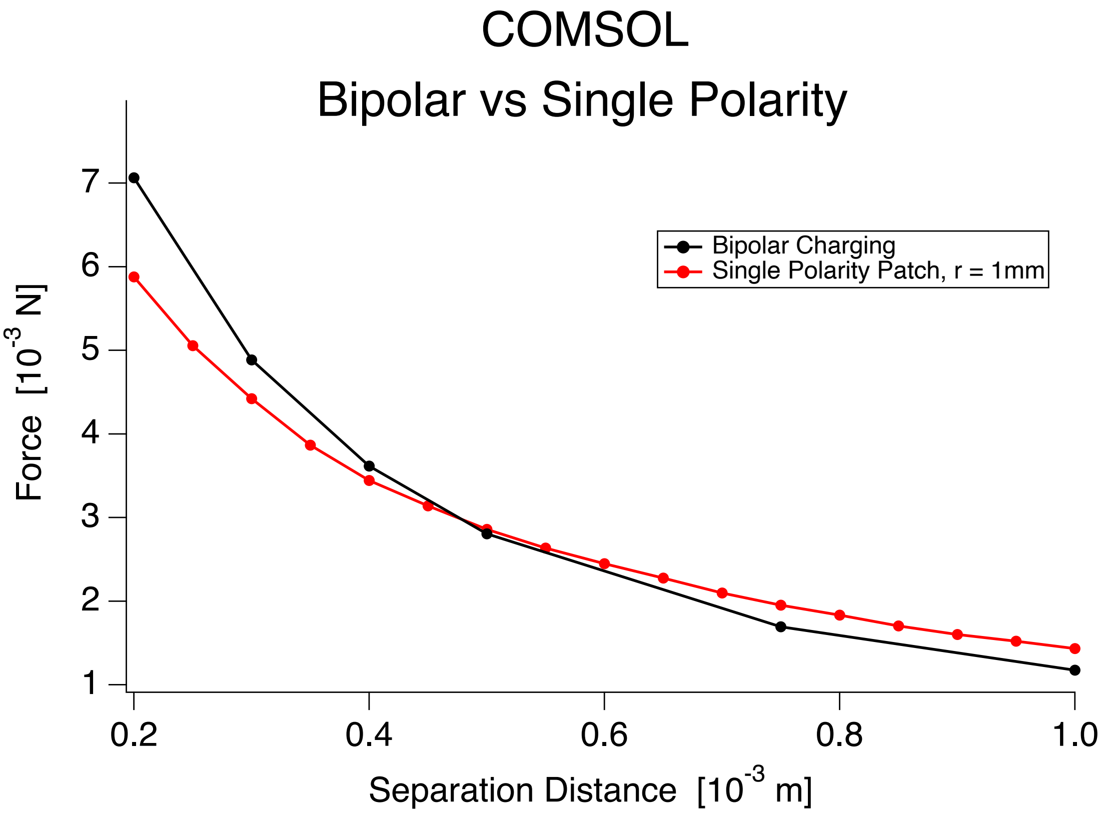

Figure 1.7: The black bipolar charging force starts above a single polarity patch with comparable charge, but falls below the single polarity patch at larger separation distances. This is the same behavior observed in our experimental data in Figure 1.6, indicating that our crystals undergo bipolar charging.

At this point we return to the experiment by the Grzybowski lab [24] and introduce a parameter of merit which is the effective accelerating surface voltage V_{eff}, which determines the energy of photon emissions from braking radiation (also referred to as Bremsstrahlung) during discharge events. For an individual patch in the mosaic the voltage is the local electric field multiplied by its effective range, which we take to be the patch length d_T, giving $V_{eff} = \frac{q_T}{2\epsilon_0 \cdot d_T}$. Alternatively, the effective voltage could be defined as the average electric field multiplied by its effective range which would now be taken to be the sample size. With either definition we arrive at the same value, which for the length scales and charge densities reported is $\sim 1\ kV$. This is significant in that even though the local charge density on the surface of the polymer is $\sim 10^{13}\ e/cm^2$, the effective accelerating voltage experienced by a charged particle traveling between the insulators' surfaces is only $\sim 1\ kV$. This is in contrast to our experiment where the COMSOL simulation reveals the 1 nC charge transfer between crystals leads to $\sim$4.6 kV potential between the insulator surfaces as shown in Figure 1.8. These surface charges can be high enough to initiate breakdown leading to x-ray emissions.

The value in analyzing force data for a range of separation distances as opposed to just the peak force is far ranging and hard to overstate, especially in complex systems. However, even for simple systems this approach reveals key information that would otherwise be missed as illustrated in Figure 1.9, which highlights the force curves nonintuitive behavior. This figure shows three force versus separation plots, two are COMSOL simulations and one is an analytic calculation. All three curves are meant to approximate the force between two uniform discs of 1 nC total charge with radius $10^{-3}\ m$. The two COMSOL simulations differ in that one takes the charge to be on the surface of a dielectric, such as in our actual experiment, while one takes the discs to be in free space. The analytic calculation is the force between a disc of charge and an on-axis point charge. There are two key features of this graph- the first is that all three curves unsurprisingly converge to the force between a uniform infinite plane and a point charge. The second is that none of the three curves plateau at small separation distances. This could be surprising if one is focused on the fact that the electric field of an infinite plane does not depend on distance from the plane. However, analyzing the equation for the field above a disc of charge reveals that while the electric field does converge to the infinite plane approximation at small distances, the slope does not approach zero. The COMSOL data shows that the slope is actually steeper than our approximation, which is expected when considering edge effects at the second disc that our point charge estimate ignores. Further, COMSOL reveals that the slope will be steeper still when considering the dielectric nature of the crystals on which the charge patches are located. The purpose of this figure is both to highlight the non-vanishing slope of the force curve so that the reader is not surprised by our data, and to show that since the slope is non-zero a single additional data point at further separation distance will immediately provide additional information about the charge distribution in the system.

This probing technique opens up the possibility to investigate contact electrification at an unprecedented level. It not only surpasses single-point measurements, but can surpass the abilities of a KPFM while measuring large areas normally limited to net-charge measurements using a Faraday pail technique. While use of a KPFM can reach atomic level resolution in ideal environments [25, 26, 27], for investigations into contact electrification the combined requirements of the need to enable materials to come into contact and then be separated and limits on how close any probe can get to the sample surface in order to prevent initiation of discharge or affecting charging behavior will reduce the practical resolution. Figure 1.10 compares a typically KPFM set up to our force-probe set up to illustrate the how our probe is much further from the sample surface and thus less invasive, avoiding the possibility of altering the charge distribution. This type of probe could be particularly useful in the event that contact electrification is driven by nucleation events at the locations of seed charges as discussed above, in which case the ability to monitor the growth and detailed distribution of charge patches could provide invaluable information into the underlying mechanism. Thus, for investigations into charge transfer between insulators the non-interfering *in-situ* probing technique presented here could facilitate the development of a long-awaited comprehensive theory behind contact electrification by enabling quick, detailed, real-time measurements of charge distribution and discharge events not previously possible.

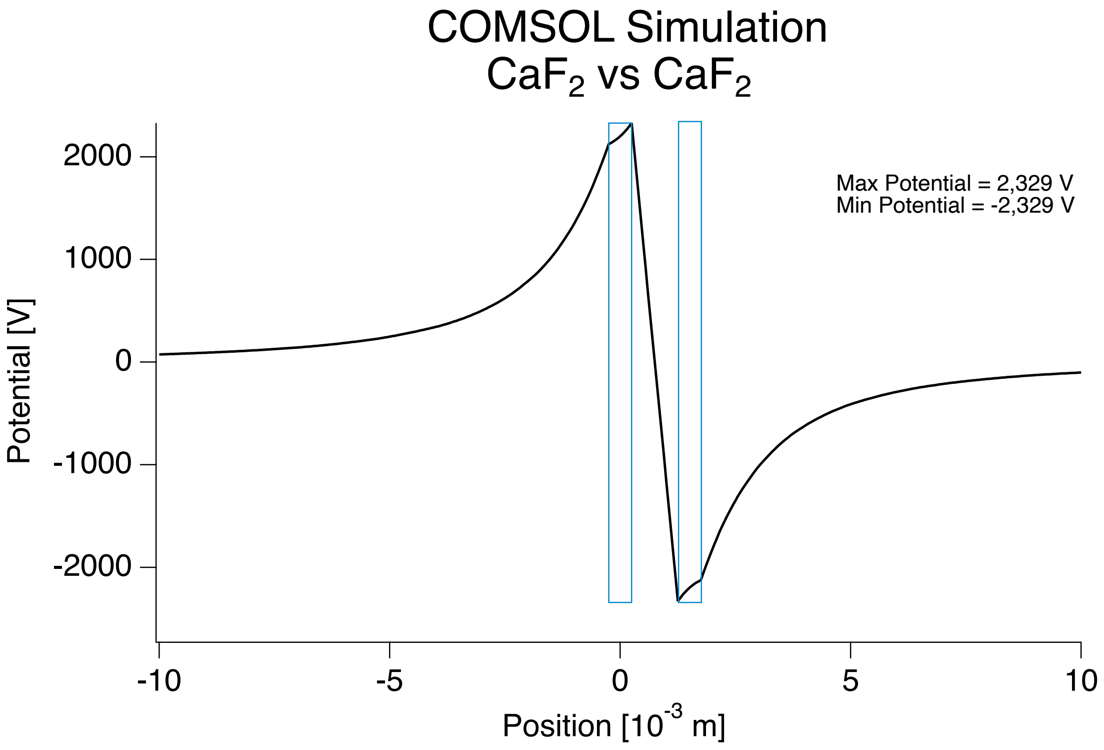

Figure 1.8: A COMSOL simulation of the potential between two single-crystals (represented by the blue boxes) of relative permittivity $\epsilon_r = 6.81$ (simulating CaF_2), with equal and opposite surface charges of $1nC$ distributed in a uniform $2 \cdot 10^{-3}$ m patch, separated by 10^{-3} m.

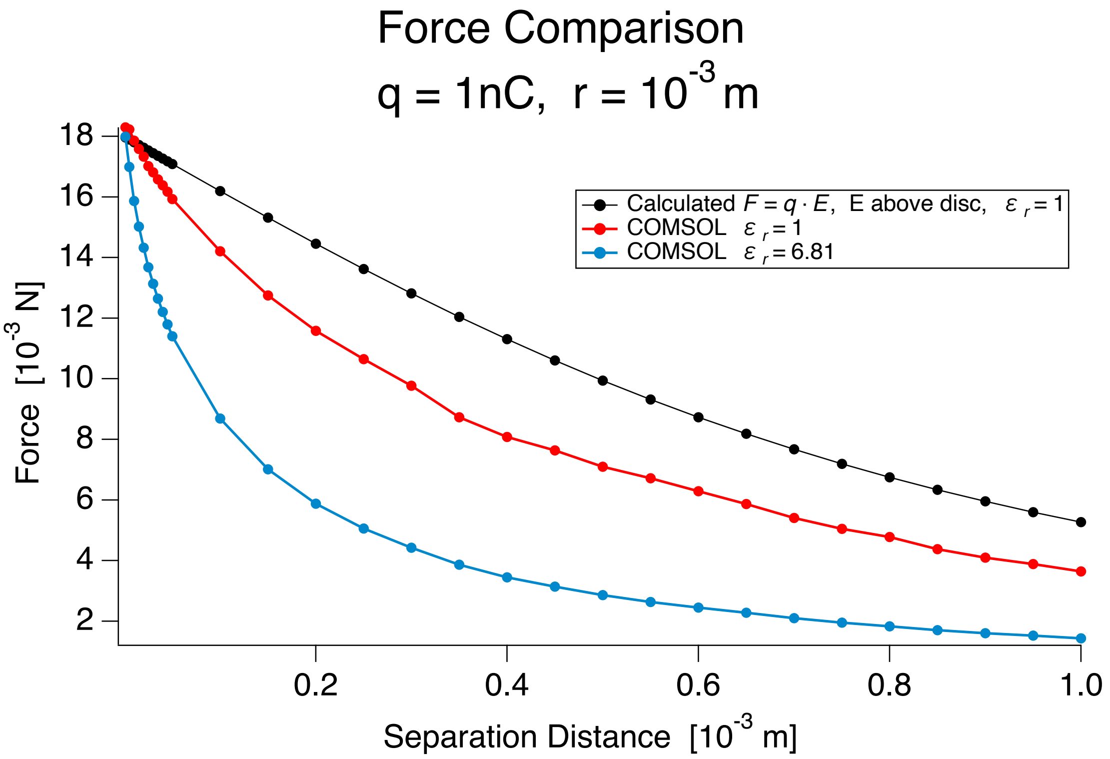

Figure 1.9: Comparisons of force as a function of distance for COMSOL simulations and a manually calculated comparison. The calculated force is very roughly estimated as follows: each crystal is assumed to have an equal and opposite uniform disc of charge with 10^{-3} m radius, the normal force between the crystals is the electric field generated by one disc multiplied by the total charge of the other, and the electric field is taken to be the on-axis field above a disc of charge, $E = \frac{\sigma}{2\epsilon_0} \cdot \left(1 - \frac{d}{\sqrt{d^2+r^2}}\right)$, with d the separation distance. Two COMSOL simulations are shown, one for the discs of charge on a material with relative permittivity $\epsilon_r = 6.81$ (to simulate CaF_2) and one with $\epsilon_r = 1$ (to simulate a patch in free space). Note that while all three curves converge to the force experienced by a point charge in the field of an infinite plane with uniform charge, the actual does not plateau for any curve at short distances.

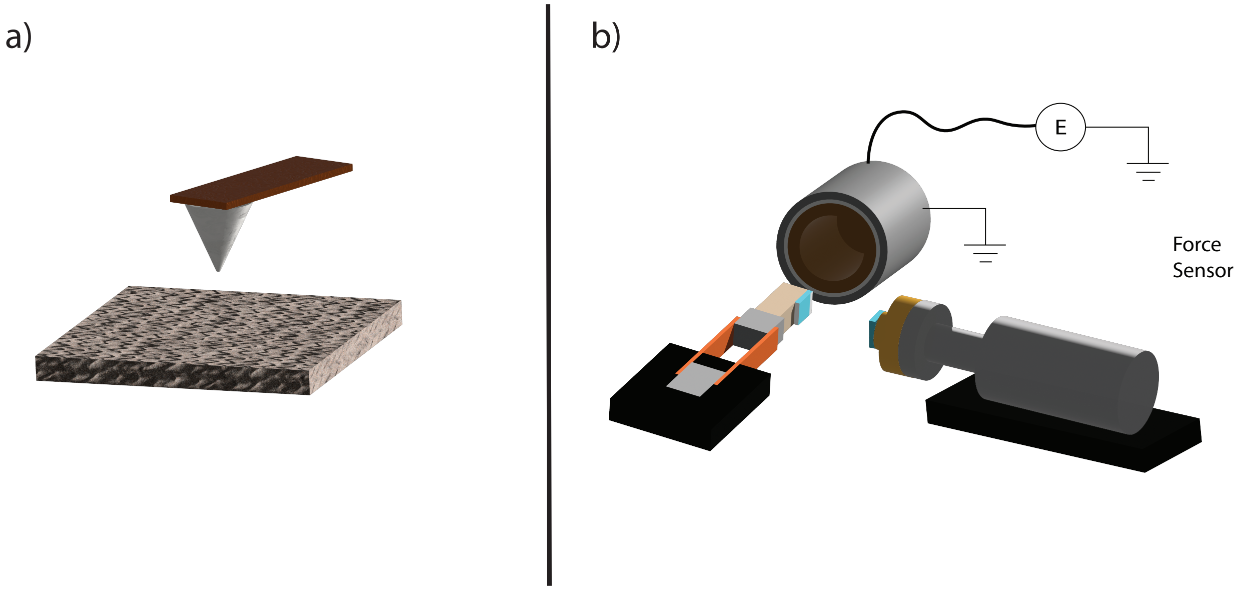

Figure 1.10: (a) A typical Kelvin Probe Force Microscope set up, the conducting probe tip must be close to the sample surface (100nm or closer) which presents the posibility of inducing discharge or altering the charge distribution via polar charge interactions between the tip and sample surface. (b) Our experimental set up, the *in-situ* force sensor is behind the crystal, avoiding any interaction with the material surface and providing real time data.

CHAPTER 2

Previous Observations of Same Material Self-Charging

Our observation of charge exchange between single-crystal samples consisting of the same material discussed above are not the first observations of self-charging between like materials. In this section we discuss other reliable experiments where like materials exchange charge, which we believe to be key to understanding the state of contact electrification and discuss their differences from our experiment.

Lowell and Truscott have shown that contact electrification can occur between two insulators made of the same material [28]. The insulators used in their study are the polymers PTFE, polystyrene, and acrylic (Poly(methyl methacrylate), PMMA). The main experiment is designed such that a sphere and a plane are made from the same material and then rubbed together to create an intentionally asymmetric contact. After this rubbing interaction any charge transfer is measured. They find that these polymers do indeed self-charge, which some readers may find unsurprising considering the contact is intentionally asymmetric, however it should be noted that this is a key difference from the lack of charging that would be expected from a conductor-conductor contact in the same set up using only one material where the equalization of Fermi levels is thought to be sole driver of charge transfer. They also run a "very crude" experiment where they show that for two planes of polystyrene, one smaller than the other, that the charge polarity tended in one direction when using the samples as received from the manufacturer, but then observe a reverse in polarity when the samples are lapped with SiC paper. In addition to these experiments on polymers Guerret-Piecourt, Bec, Segault, Juve, Treheux, and Tonck report self-charging between single-crystal Al_2O_3 crystals during an asymmetric sphere-plane contact [29]. These experiments are not included here because they are meant to demonstrate carefully controlled experiments of similar material self-charging, but rather for the simple fact that they demonstrate that these polymers and single-crystals can self-charge and this has broader implications. The fact there can be charge transfer between pieces of the same material with asymmetric contacts suggest that the nature of a rub or contact (and any asymmetries there within) in any contact electrification experiment could substantially impact any charge transfer. Further, for any other materials that exhibit similar self-charging, unless they cause of the self-charging can be shown to uniquely exist when the contacting materials are the same, the mechanisms that allows for self-charging if not controlled for can add noise to charging experiments between dissimilar materials as well, perhaps even to the point of preventing a quantitative theory of contact electrification from being established. If this self-charging behavior is unique to these materials or to polymers in general, then experiments with alternative materials could provide better data for quantitative analysis even if the magnitude of charge transfer is lower.

The observation of pieces of the same material being able to exchange charge is not limited to experiments where the samples have been intentionally made into asymmetric shapes. Apodaca, Wesson, Bishop, Ratner, and Grzybowski also ran experiments with PTFE and polystyrene as well as the additional materials polypropylene, PVC (polyvinyl chloride), and PDMS, but instead of using a sphere on plane geometry they experimented with plane-on-plane contacts so there is no intentional asymmetry [30]. They found that all of the materials they experimented with exhibited this self-charging phenomenon, although for the discussion presented here it is worth noting these experiments are with polymers not single-crystals.

Once it has been established that samples consisting of the same material can exhibit contact electrification a natural follow-up is to attempt to map the transferred charge distribution (which could give insights such as is the transfer maybe due to defects if charge in small distinct patches is observed as opposed to an unaccounted asymmetry perhaps in the bulk or in the nature of the contact if the charge is uniformly distributed). It was in one such experiment by Baytekin (H.T.), Patashinski, Branicki, Baytekin (B.), Soh, and Grzybowski that demonstrated both that for some materials the self-charging behavior actually leads to a bipolar charge distribution, and that this bipolar charge exchange can even occur even between dissimilar materials, results key to establishing any general theory of contact electrification [24]. In this experiment the authors investigate polydimethylsiloxane (PDMS), polycarbonate (PC), PTFE, silicon, and aluminum using Kelvin force microscopy to determine charge on a given materials surface before and after contact with a second sample. The authors found bipolar charging in all the materials they investigated, and found the distribution has a similar appearance to a mountain range with large mountains and valleys on a larger length scale with smaller peaks and dips on a shorter scale. For the charging they found the larger scale that best fit their data to be 0.45 μm and the smaller length scale to be 0.044 μm, and this was independent of the overall polarity and these scales were similar for their various types of electrified surfaces. It is worth noting that while the authors do report a net charge of 0.2 nC/cm^2 for a PDMS-PDMS self-charging experiment, it is not clear that the net charge is always this large and when it is the net charge could easily be the result of running experiments with polymers whose variations at the molecular level across the surface could be responsible for the net charge. Further, this density of 0.2 nC/cm^2 is small compared to the charge density of the bipolar charge patches, which the authors estimate to be on the scale of $\mu C/cm^2$. Additionally, it is worth commenting on the net charge observed on their surfaces compared to their reported length scales. If we take the authors' length scales of 0.45 μm and 0.044 μm, and assign charge to each island randomly picked from a gaussian distribution, as they do in their analysis, then if we set the standard deviation to their claimed island charge density of one elementary charge per 10 nm^2, then we expect a total standard deviation in net charge of $7 \cdot 10^{-11} C/cm^2$ for their sample with a 1 cm^2 area. This would put their observation of 0.2 nC net charge 2.8 standard deviations away from the median. If instead we assigned a standard deviation of $\frac{1}{2}$ to the reported charge density the observation would be 1.4 standard deviations away, and if we assigned a standard deviation of 2 to the reported charge density then the observation would be 5.6 standard deviations from the mean. For this reason the papers results on bipolar charging are significant, but as the net charging could be due to the variations in the polymer surface between two samples of the same material no conclusions can be drawn about a true net charge transfer between identical samples. While the paper does not prove this phenomenon to be universal it does demonstrate the effect is present for all their samples and indicates the importance of considering bipolar charging in developing quantitative theories as it pertains to the difference between total and net charge transfer and accounting for how there could be bipolar charging for dissimilar samples each of single bulk materials.

Though it is important to understand if any materials in a given experiment can exchange charge with another sample of the same material, it should be noted that self-charging is not a universally observed phenomenon. Horn and Smith conduct a series of experiments focused on charge exchange during a crossed contact of cylinders formed of silica and mica and found that there was an order of magnitude less adhesion force and no comparable charge exchange was observed between silica-silica and mica-mica contacts relative to the silica-mica contacts [31]. This observation of a lack of charging between similar materials in their experiment is further confirmed by tracking elastic deformation of the materials by electrostatic attraction which is present for the silica-mica contact but absent for mica-mica or silica-silica contacts.

CHAPTER 3

Theories of Contact Electrification

As we have demonstrated that there is experimental evidence for same material contact charging, both from our group and from previous work, we turn our attention in this chapter we discuss theories of contact electrification that predict charge exchange between single-crystal samples of the same material as observed in our experiments discussed above. We will further discuss qualities that a theory must possess in order to be compatible with our observations, and then address theories that could predict the wide variations in the magnitude of transferred charge observed in our experiments.

3.1 Theories Predicting Self-Charging

The first theory comes from a review by Wang and Wang [32], which is discussed in detail in the review of highly cited theories section, but we will address the relevant component of the review covering self-charging here. The authors reference one of their previous experiments by Xu, Zhang, A.C. Wang, Zou, Liu, Ding, Wu, Ma, Feng, Lin, and Z.L. Wang in which they contacted two samples made of the same material but with different surface curvature to examine the surface geometry effect on contact electrification [33]. The experiment is run with PTFE, fluorinated ethylene propylene (FEP, brandname Teflon FEP), Kapton, polyester, and nylon which would then be coated with Cu and mounted on an acrylic sheet of a given curvature (or flat). The authors claim the results of their experiment indicate that for contact electrification between samples of the same material but different surface curvatures, samples with concave surfaces will tend to charge positively and concave samples will tend to charge negatively. Wang and Wang argue that the results of this experiment can be interpreted as changes in the surface curvature resulting in changes in the surface energies of the material, and thus two materials with different curvatures will have different surface state energies which allows the transport of electrons once the materials are contacted. They say that the surface energy interpretation is backed up by a theoretical work of Makov and Nitzan [34]. The issue is the theoretical work is actually only for metals, not insulating polymers as in the curvature experiment, and the work relies on the fact that there is background electron density in the metal and not outside of it, this way if you contact two metals with curvature described by the same principal radii, but opposite signs such that one is concave and one is convex, then you will not get surface energy based on curvature when they are in contact, which is important since you can describe a virtual surface inside any bulk metal and should not somehow find that the energy at any given point depends on the curvature of this virtual shape. To emphasize further, the theoretical paper on metals is how the shape of the metal can affect surface energy based only on geometry, in the contact electrification experiment the material is bent and while this could affect surface states it is important that the surface states would not be different between one sample and another while they are in contact (which is when Wang and Wang argue contact electrification takes place, see previous paragraph) if they had been cut from the same material into the two shapes, so the paper by Makov and Nitzan cannot be used as support for the surface state modification interpretation put forth by Wang and Wang. Additionally, this theory of a geometric based mechanism of charge transfer cannot explain our results of same material contact electrification as our contact is between two insulating flat surfaces.

However, even without having a theoretical explanation as to why the concavity affects contact charging, if the experiment is robust it could lend insight into the nature of the charge carriers as Wang and Wang argue. Unfortunately, the experiment in question not only does not prove this, but does not provide enough statistically significant data to draw any conclusions at all. First it should be noted that for the concave-convex contact the radius of curvature is actually different for the two materials in most of the reported experiment, one has a curvature of $0.21/cm$ and the other has a curvature of of -$0.071/cm$, which opens up a range of possible influences on charging behavior such as thermal effects from different geometries, sliding has less symmetry such that a smaller patch of the higher curvature piece might contact more area of the piece with lower curvature, the stability of the surface for both the bulk material and any contaminants might be effected differently, the stress in the two materials in now different (recalling that they are not molded this way, but bent into this shape), the tendency to discharge for a given surface charge density is now different between the materials, all this among others. Even without focusing on this uncertainty the variation in all experiments is enough that no claim on the effect of curvature should be made with any confidence. These variations in charging behavior are worth elaborating on for the experiments with data reported. For the experiments with PTFE the authors run each geometry with eight different samples, and each sample is run five times with the samples being removed for cleaning between each run. The experiments with two flat pieces had polarity flips for four of the eight samples , and exhibited maximum flipping (three experiments with one polarity, and two with the opposite) in two of those. It is worth noting that in addition to the run to run polarity flipping for some of the samples, for the samples where polarity was the same in all five runs out of the four samples exhibiting this behavior two had the moving piece charge negatively and the other two had the stationary piece negatively, this type of variation is indeed only observed for the symmetric contact and is not seen for any of the asymmetric contacts. For all asymmetric experiments every sample, for a given material and geometry, has the majority of runs of the same polarity. Still, for such a small number of runs per sample and samples per geometry it is important to only draw conclusions at the level statistical analysis allows, as it is not so clear cut as if the symmetric contact appears to be random, while the asymmetric contacts are all of a single polarity, in which case more confidence could be had in drawing conclusions from a data set this size. Besides the observation of polarity flipping between samples where polarity is all of one sign, the behavior of asymmetric contacts still appears to have a large amount of variation- the experiments indicate the lack of reliability in using geometry to predict charge transfer between samples made of the same bulk material. The authors only supply data on the concave-convex contacts for the materials other than PTFE, but the fact that for every one of these materials exhibits polarity flips for at least half of their samples strongly suggests that contact electrification between samples of the same material cannot be explained by geometry alone. In fact if attention is paid not just to polarity but also the magnitude of charging in each of the experiments, then it becomes clear that a geometry argument based on surface states is incompatible with the data. If, as the authors suggest, a shift in surface states due to geometry were responsible for the charge transfer then we would expect no charging for symmetric surfaces. While of course no two surfaces are perfectly symmetric the shift in surface states should be correlated with the geometric deviation from each other, such that a curved surface will charge more strongly when contacted with a plane surface compared to a plane surface contacted with a plane surface. In the reported experiments the magnitude of the charge transfer does not follow such a correlation and for the two surface with the most different geometries (convex and concave) two of the eight samples still exhibit polarity flips. It should be expected that even for the high curvature samples there are microscopic variations in the surfaces, but if this influence is large enough to not only completely reverse the direction of charge transfer but to do so in such a substantial method as to give a polarity flip with equal magnitude, as is observed for various samples, then it does not make sense to consider the bulk geometry as a reasonable predictor or driver of charge transfer. To offer even more support of this attention should be paid to the fact that maximum polarity reversal occurs in 1/3 of samples for every material with the exception of PTFE, demonstrating a substantial inability to predict charge transfer from the geometry of similar materials. Further, when investigating the effect of force on the voltage between the materials (charging was too low to measure at low contact force) they found for one PTFE sample with two convex surfaces contacting each other that the voltage increased with increasing contact force, and this same result was found with two flat surfaces contacting each other. However, in a second identical experiment with the two convex surfaces they voltage did not increase with increasing force and further they found a polarity reversal between the contacts up to $8N$ and those $10N$ and above. Even more, they found for a different PTFE set up still with two convex samples, but where the curvature of one was changed compared to the previous two experiments, that there were two polarity reversals where the voltage for forces between $5N$ and $20N$ was of the opposite sign compared to when the force was $2N$ or less and when the force was $25N$ and higher. It might be reasonable to expect that if contact electrification charge transfer is mediated by electrons in a manner such that the direction of movement is determined by the surface states of the material as Wang and Wang argue, then there could be some dependence on the applied force via the actual contact area at both the macroscopic and molecular level, any changes in surface state energies, changes in the nature of any rubbing and related effects such as relative temperature differences, among others. However, the fact that two experiments with all controlled parameters identical to each other still gave not just quantitively, but qualitatively different behaviors makes it impossible to draw any conclusions about the charge carriers from these experiments. Even a claim about multiple mechanisms simultaneously driving charge transfer in different directions, with varying relative strengths depending on the applied force would be dubious considering the lack of repeatability from one experiment to another. Further the authors of the experiment go as far as arguing that the observed polarity flips and lack of repeatability might be due to material transfer, but this goes entirely against their case for charge transfer being solely mediated by electrons. Such experiments may be used to put limits on relative contributions of bulk and surface effects, but when lacking repeatability the results should not be interpreted in a manner supporting any single charging mechanism or charge carrier.

While there are other experiments that have reported same material charge transfer, there are no prevalent theories that explain why charge transfer should occur between two crystal samples of the same material. We will review highly cited theories of contact electrification in a later section, but none of them provide insight into the significant charge transfer between identically shaped single-crystals materials in our experiments.

3.2 Theories on Contact Electrification

Here we give a brief overview of the characteristics a theory must possess if it is to explain contact electrification based on the key experiments above. At this point we will not present highly cited theories of the charging phenomenon as there is not a consensus or dominating theory at the time of writing and we don't believe any are supported by enough evidence to stand behind, however we do present a critique of them in Section 5.3 Highly Cited Theories.

With a phenomenon of charge transfer such as contact electrification a complete theory must include both the nature of the charge carrier involved in the transfer as well as the driving force to move those charge carriers from on point to another. The possible charge carriers are electrons, ions, or bulk material and can be either native to one of the intentionally interacting materials or from ambient gasses or liquids present in the environment. Any theory will require one or more of these carriers and one or more force mechanisms to move these carriers. The force mechanisms might be most easily understood in an energy picture, but this energy picture must be sufficiently detailed with any potential barriers and what determines the energies of the charge carriers before and after charge transfer has occurred. If there are energy barriers a theory must adequately explain where the energy comes from to overcome such barriers. In general if the underlying mechanism is sufficiently described by a theory, it should be able to predict the effect of charging various parameters such as the amount or lack of rubbing, the temperatures of the materials, relative effects of the surface and bulk, effects of surface contaminants and the ambient environment, the rate of charging and peak charge transfer, the nature of charge distribution after contact, whether the charging mechanism is deplete-able and if it is then if it can be replenished, among others. So a complete theory should be simple in its identification of charge carriers and driving mechanism, but for it to be complete and verifiable it requires strong predictive powers.

In addition to these characteristics, the theory must be accountable to observations of same material charge exchange. To be clear, it is not necessary that the theory attributes charge exchange between samples of the same material to the same underlying mechanism as charge exchange between dissimilar materials, but in the case a theory does rely on two fundamentally different mechanisms then the theory must be able to explain why the mechanism that drives the self-charging can only play a role in the case of two samples of the same material contacting but not in the case of two dissimilar materials, as our experiments presented above make clear that the magnitude of self-charging when it does exist can be as large as the magnitude of charge exchange in the dissimilar material case. Further, our experiments demonstrate there can be significant variation in the magnitude of self-charging between one type of crystal pair and another, and that even within experiments between one type of crystal pair there can be changes in the polarity of charge transfer from one run to the next, and any theory of contact electrification must be compatible with these observations. If a theory attributes charge exchange between like-materials to some asymmetry in the contact, then it must provide how this affects charge exchange between two different types of crystals and address the observation that for certain dissimilar crystal pairs there tends to be a fixed polarity in the charge exchange. A related observation that must be addressed is that the charge exchange between like-materials does not seem to vary wildly from contact to contact. That is, although the polarity of charge exchange might vary from run to run, or even change directions within a run, the data does not appear as if a coin is flipped each contact randomly determining the polarity (this is shown quantitatively in our results section), but rather that charging tends to stay the same from one contact to the next, and any reversal in charge polarity is proceeded by a reduction in the magnitude of charge exchange over several contacts. Previous observations of charge exchange between samples of the same material when the materials were asymmetric or were polymers added a challenge to theories of contact electrification, but possible variations in sample surfaces allowed for theories to simply attribute the results to some hidden surface condition or asymmetry without addressing the results in detail. Our results with symmetric samples of single-crystals smooth at the angstrom level require accountability at a significantly more explicit level.

3.3 Surface Reconstruction

The variability in the magnitude of charge transfer observed in our experiments both for charge exchange between samples of the same single-crystal material and between samples of different crystal types naturally leads to a desire to determine the importance of the exact nature of the crystal surfaces during charge exchange. Particularly, does the surface have different properties from the bulk crystal, and how sensitive are these properties to ambient conditions, contaminants at the surface, and impurities introduced into the surface.

Our investigation into contact electrification between materials made of single-crystals could provide a more reliable route to understand the mechanism that drives charge transfer, and is particularly useful when attempting validate theories based on band energies. However, if the goal is to formulate a theory that depends on the crystal structure of the materials involved it is important to take into account any experiments that suggest the interacting surfaces could have different structures than their respective bulk materials. That is, does the surface follow the same atomic structure as if the bulk crystal pattern were to simply terminate, or does it take on a new structure from the asymmetry between a bulk crystal on one side of the surface but absent on the other, or even from interactions with the ambient environment. If one can select for materials that do or do not have surfaces different than their bulks and if one can change the surface structure without changing the bulk then a determination can be made as to if the charging mechanism is driven by the bulk material or by the interacting surface. It is known that materials such as clean silicon [35] and gold [36] will exhibit surface reconstruction in vacuum, but experiments by Siretanu, Ebeling, Andersson, Stipp, Philipse, Stuart, van den Ende, and Mugele have further shown that for certain materials the surface reconstruction is not simply universal depending on the plane that the crystal is cleaved, but in addition to depending on materials present at the surface can actually depend on the concentration of those materials [37]. Their experiments focus on gibbsite nanoparticles (α - $\mathrm{Al(OH)_3}$) on a silica surface, surrounded by a salt solution. For a given experiment they will use one of NaCl, KCl, $\mathrm{CaCl_2}$, and $\mathrm{MgCl_2}$ as their salt, and then vary the concentration. They use atomic force microscopy to not only show that the surface will reconstruct differently depending on the salt solution, but they are additionally able to image a gibbsite surface showing spatial domains of both the high concentration surface structure and low concentration structure next to each other when the solution is at an intermediate concentration. This experiment indicates the importance of understanding the exact surroundings of a crystal surface for developing any theories wherein the driving mechanism behind charge exchange is dependent on surface structure. This includes accounting for the cleanliness of experiments run in vacuum, as water or impurities in the system could change the nature of the crystal surface, leading to different results not only between ab initio theory and experiment, but even between two seemingly identical experiments.

On a related note McKee, Walker, Nardelli, Shelton, and Stocks present a case for the importance of taking into account interfacial structural variations when determining the band diagrams and charge distribution at the interface between two materials [38]. They focus on the Si-BaSrO interface, but make an argument that applies broadly to the interface between two dissimilar crystals. They show the importance of not treating the charge distribution at the junction as simply a superposition of the bulk materials but that the actual structure needs to be taken into account and leads to changes in the electro-static conditions at the boundary including the induced charge distribution. Wang, Satio, Chen, Mastubara, Ueno, Kawasaki, and Ikuhara are able to explicitly image such a boundary reconstruction for the interface between $CuScO_2$ and $MgAl_2O_4$ crystals at the atomic level [39]. Although these two papers do not address the case of dissimilar crystals prepared separately, then brought into contact and separated again, these papers do lend further reason to believe surface reconstruction could occur when two crystals are brought into contact and further that the reconstruction could play a key role in charge transfer between the materials. Thus if contact electrification is not determined solely by the bulk materials involved in the interaction, but depends on the interacting surfaces as well then it is reasonable to believe knowing surface structure at the interface of the materials at the time of contact could be critical to understanding the mechanism behind charge transfer.

These observations demonstrating crystal surface reconstruction to be highly sensitive to the exact local conditions could provide an explanation as to why large variations in the magnitude of charge transfer between one experiment to the next, or one run to the next exist, and could even provide a possible route to understanding charge exchange between samples of the same material.

CHAPTER 4

Surface Reconstruction and Charge Transfer

The fact that surface reconstruction can play a critical role in electric properties at an interface as well as the physical reconstruction and that this surface reconstruction is so sensitive to ambient conditions suggests that this phenomenon could be critical to understanding contact electrification, both between samples of the same material and between dissimilar materials. We discuss here how surface reconstruction during contact and after charge exchange could lead to the observations in contact electrification experiments.

In addition to surface reconstruction, bulk crystal structure can change under pressure. For example, SiO_2 can undergo structure changes at pressures as low as 10 GPa [40]. For our experiments we contacted crystals under low applied force, which would result in a pressure in the range of 10 kPa if the force were applied perfectly evenly over the entire 1 cm × 1 cm crystal surface. However, at the molecular level local pressures could far exceed this value even with our surface smoothness on the angstrom level, depending on the exact contact. This combined with surface reconstructions sensitivity to changes in the ambient environment including contaminants and the presence of other crystals makes it likely that there is some sort of reconstruction occurring, both before and importantly during crystal contact within our experiments.

Surface reconstruction could contribute to charge transfer through several possible routes. The first would be that local conditions from one point on a crystal surface to the next could lead to each crystal face having a range of reconstructed surfaces that vary from one area to the next. Upon contact, the physical parameters of each reconstructed area could lead to bonding and then fracture as the crystals are separated. This could lead to material transfer from on crystal to the other. While the material in the transfer could contain net charge, the fact that repeated contacts tend to increase the net amount of charge transferred would seem to indicate that the primary mechanism of charge transfer is not via this material transfer, as after fracture each crystal surface would either remain constant or newly reconstruct, and it is not obvious that this should then allow for new surface reconstructions to form that when then fracture in the same away as the original fracture which would mean the charge transfer from one contact to the next should not be expected to always carry the same polarity. However, even if the initial contact and fracture is not the primary mechanism of charge transfer, it could provide a path for charge transfer in succeeding contacts, and this exemplifies the importance of not only identifying if material transfer occurs in a contact electrification experiment, but needing to go further to prove if the material transfer is the actual charge transfer, is an independent coincidence, or if does not carry the charge but allows for future charge transfer.

Another possible route that surface reconstruction could contribute through charge transfer is by affecting charge states in the surface of the materials. Since surface reconstruction can affect electric properties of the materials, it could raise the energy of electrons in one surface relative to the other and allow for electrons to flow from the higher energy surface to the lower. This could be consistent with observations of bipolar charging as the surface reconstructions could vary from one point on the surface to the next, and because the actual flow could depend on the reconstruction during contact which could vary from one point to the next based on the combination of the local reconstruction on both sides of the interface, on the local pressure, and any contaminants in the contacting area. A challenge for this interpretation is charge transfer seems to increase from one contact to the next, but does not increase from changing the contact from one second to one minute (it is time independent on the scale of seconds and larger), where as the electron flow should only depend on having enough time for the charge to move, and not benefit from multiple contacts. If the exact position one crystal surface contacts the other varies from one contact to the next this could provide additional charge transfer, but based on the bipolar charging this should be random, in contradiction to the observation that charge transfer tends to maintain its polarity from contact to contact, even for samples of the same material.

Perhaps it is more likely that the charge transfer arises from some version of a charge nucleation event and the surface reconstructions role is either just to provide the seed charge or in carrying out the nucleation from seed charge that happens to be on one surface or the other. C.L. Fu and K.M. Ho provide a theoretical argument for external charge induced surface reconstruction of a Ag (110) surface [41], while J. Kraft, M.G. Ramsey, and F.P. Netzer experimentally show how Si surface reconstruction can be influenced by an electric field [42]. Thus some initial seed charge could cause a local surface reconstruction that could favor additional charge transfer, either by changing surface state energies or by physical material transfer from fracture, then this additional charge could invoke further surface reconstruction creating a cycle where each successive surface reconstruction amplifies the original charge signal and propagates further charge transfer of the same polarity. This would be consistent with temporal charge saturation on any given contact, but increased charge transfer over repeated contacts, and with the tendency of net charge transfer to maintain the same polarity from contact to contact. Further, this allows for charge transfer between like materials from initially random seeds or local surface contaminants, while also supporting tendencies for pairs of dissimilar crystals to favor certain polarities of charge transfer based on allowed surface reconstructions and still allowing for variations in magnitude from non-uniformity of the crystal surface and even the occasional polarity flipping given rare conditions where significant excess seed charge on surface could dominate the normal direction of charge flow that exists when seeds charges are more closely uniformly distributed. If there is another method of propagating a charge nucleation event the surface reconstruction provide the initial seed charge from electron or material transfer during initial contact, and is consistent with bipolar charging observations as these seeds would vary at the same degree that surface reconstruction varied based on ambient conditions before and during the initial contact.

More experimental work is needed to solidify understanding of the role (or lack there of) of surface reconstruction in contact electrification, but it provides an alternate path towards a complete theory of contact electrification from the highly cited theories discussed in a later section. Whether or not surface reconstruction plays a role, an investigation into the possibility of a charge nucleation event being responsible for the pattern of charge transfer in contact electrification would be prudent based on the consistencies discussed above.

CHAPTER 5

Assessment of The Current State of Contact Electrification

This chapter first covers the key experiments the author believes to be relevant to establishing a complete theory of contact electrification that have not been covered in previous chapters. Then we will present experiments that do not lend key insight to the mechanism behind contact electrification, but could be relevant to a reader developing their own theory where null or ambiguous results can help to refine details or eliminate certain possibilities for the proposed mechanism of charge transfer. Next we provide a critique of the most highly cited papers presenting theories of contact electrification and of highly cited experimental papers that contain flaws that prevented them from being included in the key experiments section of our work. As will become clear here drawing conclusions beyond what is reasonable from their referenced experimental evidence is ubiquitous in the theory papers, while many highly cited experiments do not properly control for conflating variables and there is a widespread tendency of avoiding repeating experiments to the point required for statistical significance and often present no evidence of repeatability at all.

Within the highly cited theories and experiments covered here there is a recurring interpretive error that occurs frequently enough to merit addressing upfront so we do not have to repeat the same explanation of the mistake every time that it arises. To start, note that for any charged material that is not maintained at a given fixed voltage via some apparatus (including simply grounding a material with finite conductivity) then the net charge on that material can be neutralized in six ways- if the net charge is originally negative by the addition of positive ions [43], by the removal of negative ions, or by emission of electrons, and conversely if the net charge is originally positive then by the removal of positive ions, the addition of negative ions, or by electron bombardment. Electron emission and electron bombardment are applicable to all materials as electrons will naturally neutralize positive ions and all materials contain electrons that can be freed with appropriate energies (whether energy is provided by electric fields, heat in thermionic emission, or photons in photoelectric effect), the addition of ions of either charge similarly has broad applicability as they are naturally attracted to the net opposite charge of the material, only removal of ions should have a tendency to show a strong dependence on the exact surface chemistry of the materials involved. The significance of this is that showing that one of these methods (especially the widely applicable ones) can neutralize or dissipate the net charge on a material after contact electrification is not on its own indicative of the charge carrier species. For example, if electrons are the charge carrier then exposing the negatively charged material to high energy photons may release electrons via the photoelectric effect, and in the same way if positive ions are the charge carrier then the negatively charged material that owes its net charge due to the removal of those positive ions, can still be neutralized by emission of electrons again via the photoelectric effect. This applies equally well to the neutralization methods mentioned above with the exception of ion removal, and thus those methods should not alone be used as evidence as to the charge carrier responsible for charge exchange in a given interaction. This can be summarized in the following postulate:

Postulate 5.1 *The ability of a given charge carrier to reduce the magnitude of net charge on a given material does not imply that the same carrier species was involved in the original charge transfer to or from the material.*

This is closely related to another possible interpretive error, that is perhaps more obvious when explicitly stated, but could occur when an investigator is not careful when using results of conductor-insulator contact charging to draw conclusions about the mechanism behind charge transfer between insulators. This error is that being able to force a charge onto an insulator, of any carrier type including positively or negatively charged ions or electrons, does not indicate that the added charge carrier is responsible for contact charging in interactions between that insulator and another given insulator. Again, stated this way the statement might seem obvious, and applied for example to an experiment where an electron beam is used to charge a material it might be completely clear that this result should not be used as evidence that the material normally exchanges charge by electrons. However, it is equally important to note that it applies for example in an experiment where a negatively biased conductor contacts an insulator and the insulator becomes negatively charged. In such an example the result cannot be used as evidence that electrons are the charge carrier in contact electrification between that insulator and another, for we know that with large enough negative bias electrons will be emitted from the conductor and if they happen to collide with the surface of the insulator then it is possible they will become bound to the surface. This could also be true if an ion gun emitted negative ions towards the insulator's surface, thus neither experiment reveals information about contact electrification between the insulator and another insulating material. This can be summarized in a postulate closely related to Postulate 5.1:

Postulate 5.2 *The ability of a given charge carrier to produce a net charge or increase the magnitude of an existing charge on an insulator does not imply that the same carrier species is involved in all or any charge transfer between that insulator and another given material.*

5.1 Key Experiments on and Related to Contact Electrification

This section covers the experiments the author believes to be key and reliable in establishing a theory of contact electrification.

When determining the underlying mechanisms behind charge transfer between insulators perhaps the most critical variable to determine in any given experiment is the charge transferred between materials. One method to determine the amount of charge transferred is direct measurement via a Faraday cup, that is to insert the material holding the charge into a grounded conducting cavity and then to integrate the current that flows from ground into the cup to calculate the image charge formed which can be combined with the geometry of the configuration to determine the charge originally contained by the material of interest. It is critical to note, though, that the measured charge is not solely dependent on the nature of the charging, but also depends on the nature of the discharge. Kwetkus, Gellert, and Sattler demonstrate this key result by showing a change in the maximum observed charge as a function of ambient pressure [44]. Though their experiment specifically investigates discharge after contact electrification between epoxy resin and copper in helium and dry air, it is crucial to apply this knowledge when interpreting data related to charge determination in any contact electrification experiment. That is, any measured charge transfer after material separation depends on both the charging mechanism and on the nature of any discharges within the system. This has profound implications for developing any quantitative theory of charge exchange and demands that ambient conditions must be taken into account when comparing experiments, not just in how they could influence the charging mechanism, but also in how they affect discharge. Discharge during contact electrification experiments has been observed by other groups as well, such as in the experiments of Horn and Smith on charge exchange between silica and mica [31]. It is worth pointing out that the in the experiment by Horn and Smith the authors used the force between the samples as a secondary probe to confirm the charge transfer and monitor any discharges.

In the same paper Kwetkus, Gellert, and Sattler verify their discharge theory via a photomultiplier tube connected to a storage oscilloscope [44]. The reason this is worth mentioning separately from their main thesis is it forms the basis for creating a method to confirm charge calculations and potentially lend insight to and confirm charge distributions as well. Though these authors stop with verifying discharge, one could set up the experiment in such a way that the light emitted is captured and the energy distribution is analyzed. In the case where the light captured is in x-ray range from braking radiation of electrons and the system is in moderate vacuum the potential between the crystals could be determined which in turn can reveal information about the total charge and charge distribution.

Harper has argued that observed contact electrification between dissimilar metals is consistent with the theory that the charge exchange in the metal-metal case is driven by equalization of the fermi levels in the two materials [45]. Lowell and Rose-Innes describe this process in detail including the effects of tunneling as the materials are separated, where at very small separation distances the electrons can move from one metal to the other even across the energy barrier of the vacuum separating the materials [46]. They show that the Fermi levels are related to the work function of each metal. The actual strength of the evidence supporting Harper's theory is discussed in the highly cited theory section, however if the theory is correct then it is possible in the insulator-insulator contact charging case there is an analogous mechanism depending on relative potentials that is fully or partly responsible for charge transfer, and it becomes important to identify anything that could substantially impact these potentials. Chelvayohan and Mee indeed show that the work function of silver (which varies by face) can change by 0.4 eV depending on the surface cleanliness [47]. Trigwell, Mazumder, and Pellissier examined the work functions of insulators in atmosphere at 40 % relative humidity using UPS (ultraviolet photoelectron spectroscopy) while monitoring surface contamination using XPS (x-ray photoelectron spectroscopy) and were able to establish effective work functions for their materials, albeit with the materials showing substantial contamination [48]. There is no immediate reason to believe an analogous effect on work function from observed contamination would be absent in the case of insulators, thus when interpreting experiments not only does any reconstruction due to ambient conditions and the presence of the contacting material need to be taken into account, but any contaminants that can reach the material surface must be considered in theories with work functions. Importantly when deriving a theory the values for work function used should have been measured under the same conditions as were present during the actual contact electrification experiments used to determine charging polarity and magnitude.

Shaw published in 1917 a "tribo-electric series", an ordered list of materials in which he states that any first material when rubbed with a second further down the list will cause the first material to charge positively [49]. In this work he references previous such series dating as far back as 1759, with the various series show similar general ordering trends but where individual elements will be in different relative positions from one series to the next. The importance of this publication that merits its placement in this section is not the specific results and order of this reported series or their reliability, but the idea that here has been a long standing belief that certain materials will charge with a specific polarity relative to other materials, and that there is reasonable evidence across centuries to support this belief. Though there are variations from one series to another, there are also materials that are consistently reported in the same order. This is a critical observation in that it indicates that despite many materials sensitivity to exact surface and experimental conditions there is in at least some material combinations a driving mechanism behind charge exchange that is robust and repeatable in a qualitative way. Additional evidence as to the consistency of certain charge exchange interactions comes from H.T. Baytekin, B. Baytekin, Soh, and Grzybowski who conducted experiments with PTFE (polytetrafluoroethylene, brand name Teflon), polycarbonate, polydimethylsiloxane (PDMS), and Silicon wafers in ambient atmosphere (about 40% relative humidity) and in paraffin oil and found that charge transfer also occurred under oil and of the same polarity as the atmosphere experiments despite the completely different local conditions[50]. Further, these observations set up a path to understanding the number and nature of these mechanisms. If all series show the same repeatable order, especially in a range of material and ambient conditions, then there is an indication of a single dominating charging mechanism. If the order frequently changes between two similar experiments, it could indicate a strong sensitivity to experimental conditions and exact sample preparation which tends towards theories where this is an expected result of the specific mechanism. If contrary to the above belief that a strictly ordered series is achievable there are frequent observations where a subset of three materials in a series show a cyclical charging behavior, then this would suggest that there are multiple charging mechanisms such that their relative contribution varies with the exact materials involved. In this situation it would be possible to have one charging mechanism dominate for two of the combinations, but a second mechanism dominates for the third combination leading to the cyclical behavior. Thus Shaw's work is key here both in that the existence of a reasonably repeatable series suggests there is reason to believe a general theory of contact charging can be established rather than that charge transfer is so strongly dependent on the exact combination of materials as well as on experimental conditions and material preparation that a broad theory is unlikely to be established, and that it provides a path through careful observation of the robustness and order strictness to make substantial gains in understanding the forces driving charge exchange.

Baytekin (H.T.), Patashinski, Branicki, Baytekin (B.), Soh, and Grzybowski have additionally given evidence that material transfer may occur in certain contact electrification interactions [24]. In their XPS measurements of PTFE and PDMS before and after contact with each other it is clear that elements of each material become present on the other and indicates material transfer has occurred. Further, using confocal Raman spectroscopy the authors provide evidence that chemical reactions take place at the surface of PDMS when two samples of the material of been brought into contact with each other, specifically there are indications of increased oxidized molecules after contact. A similar observation was made by Piperno, Cohen, Bendikov, Lahav, and Lubomirsky using XPS for contact between acrylic and PTFE, with the PTFE acquiring at least 25% of a monolayer from the acrylic and the acrylic acquiring 25 - 60% of a monolayer from the PTFE [51]. Though the ability of material to transfer needs to be investigated for any individual species used in an experiment, especially harder materials, the fact that this can happen for at least some materials that exhibit contact electrification and that chemical reactions can take place even in experiments with like materials contacting each other, demonstrates the importance of taking these two phenomenon into account when determining the mechanisms that drive contact electrification.

The key points established by these experiments are that (1) a variety of insulators can exchange charge with each other, (2) this charge exchange can happen in a range of environments and with different preparations of the materials' surfaces, (3) the surface of a material may take a different form from the bulk with many materials exhibiting surface reconstruction and this reconstruction may depend on the ambient environment at the material surface, (4) in experiments regarding the photoelectric effect which involves charge transfer from a material into vacuum the energy required to remove the charge can depend strongly on surface cleanliness and on crystal orientation for a single-crystal material (5) samples formed from the same material may exchange charge with each other even when there is no intentional asymmetry in sample preparation or in the contact between materials, (6) both similar and dissimilar materials may exhibit bipolar charging and this is the extreme example of observations of non-uniform charge transfer across the material surface. Taken together these key experiments provide the basis for beginning to put together a theory of contact electrification and lend insight to which other experiments should be undertaken to finish building a quantitative, unambiguous theory.

5.2 Additional Experiments

Z. Zhang, Z. Wang, Chen, Feng, Dong, Zhou, Z.L. Wang, and C. Zhang conducted experiments with semiconductors, specifically examining the effect of doping on contact electrification [52]. In their experiments they work with GaN and Bi_2Te_3 and show that for both pBi_2Te_3-nGaN and nBi_2Te_3-pGaN the polarity of voltage and direction of current generated during rubbing is the same suggesting that contact electrification maintains the same charge transfer polarity with GaN charging positive relative to the Bi_2Te_3, independent of the direction of the p-n junction. We do not propose that this experiment is rigorous enough to be interpreted as saying that in contact electrification between p-type materials and n-type materials that the doping has no effect, but the fact that it is not the dominant under certain circumstances is worth considering. It should be noted that while another experiment had been conducted by Xu, Zhang, J.Y. Wang, Liu, J. Wang, and Z.L. Wang using p-type Si contacting n-type Si the experiment had an asymmetric contact that does not appear to have been controlled for by exchanging the two types of Si so similarly we do not draw broad conclusions from the experiment, but can say there are circumstances in which rubbing a p-type semiconductor with an n-type semiconductor results in an observed current that could be interpreted an the n-type charging negatively relative to the p-type [53].

There was an interesting experiment carried out by B.D. Terris, J.E. Stern, D. Rugar, and H.J. Mamin in 1989 where they ran an experiment using an AFM with a Ni tip contacting a PMMA sample and observed bipolar charging when no voltage was applied to the tip

[54]. The bipolar charging was observed on a scale of several micrometers, with variation in the distribution and net charge from sample to sample. These observations were made with a metal-insulator contact in atmosphere, so it is absent from the Key Experiments on and Related to Contact Electrification section due to uncertainty in its relevance to insulator-insulator charging and the unknown contribution of the ambient atmosphere, but it is a well executed experiment and the results are worth taking into account before drawing conclusions from any experiments where an AFM is used to deposit it charge, as the bipolar and variable charging can affect force measurements and measurements of the net charge or potential above the sample.

Shuyao Li, Jinhui Nie, Yuxiang Shi, Xinglin Tao, Fan Wang, Jingwen Tian, Shiquan Lin, Xiangyu Chen, and Zhong Lin Wang ran an interesting experiment studying contact electrification between polymers and metals and then between the various types of polymers [55]. The study was specifically investigating how polymers with different functional groups, but all contained carbon back bones would affect contact electrification. The materials investigated were PP, PE, PVA (poly(vinyl alcohol), PVC, PVDF (polyvinylidene fluoride), PTFE, and FEP (fluorinated ethylene propylene). The PE has two H on every C and the PTFE has the same structure but with two F on each C. The PVDF alternates between these two, with two F on one carbon and two H on the next. The PP and FEP are similarly related as the PE and PTFE where now the PP has a CH_3 functional group attached to every other C instead of a H, and the FEP has a CF_3 functional group on alternating carbons instead of an F and the FEP rotates between this structure and the PTFE structure in sections where as the PP follows its pattern reliably. Then the remaining two compounds are are similar to PP but with PVA having an OH group in place of the CH_3 and the PVC having a Cl group instead. Although the polymers can in some cases have extremely different physical properties (PVA is water soluble while PVC is not), if the experiment is adequately controlled for the comparison of these polymers where the backbone is the same could provide insight into the driving mechanism behind contact electrification. The experiment is set up so the polymer is mounted on a metal electrode which is then attached to an electrometer which has its other side connected to either the mounting of another polymer or directly to the metal in the metal-polymer experiments. Thus, when the materials are contacted and then separated charge will flow to the electrodes to screen any fixed charge on the polymer films. If the functional group is what uniquely determines the charge transfer and it is electron mediated, and the experiment is repeatable such that using different samples of the same materials result in the same charge transfer each time, then it would be reasonable to expect that in polymer-metal contacts the PVDF would exhibit a charge transfer equal to the average of the PTFE and PE transfers, as it has half its carbons have the two F of PTFE and half have the two H of PE. The results for these three materials contacting an Al film are reported as the PE becoming positively charged by 10.9 nC, the PTFE charged in the opposite direction at -15.8 nC, and the PVDF charged in the same direction as the PTFE at -6.2 nC. While this is somewhat close to the average of -2.5 nC (at least the polarities are the same), the paper doesn't show the variation in measured charge between various samples (for a given sample pair the measured charge on repeated contacts does not appear to change within the resolution published) so it is not obvious that -6.2 nC measured charge is actually in agreement with the -2.5 nC average that would be expected with an electron carrier charge transfer driven by the electronegativity as the authors suggest. It is also taking a closer look at the charge transfer between these polymers directly, instead of comparing how they interact with the Al foil. In their experiment when PE and PTFE are contacted with each other, the PE charges positively by 13.7 nC. If instead these polymers are each contacted with their hybrid polymer PVDF a charge transfer of 9.7 nC is observed for the PE (with the PE positive) and a charge transfer of 6.2 nC (with the PTFE negative). If the only factor in this charge transfer was the change in energy when the H or F received or lost an electron, then it would be reasonable to expect a similar additive relation as is seen with standard electrode potentials. This would imply that the charge transfer between PTFE and PE should just be the sum of the transfer of PTFE to PVDF and PVDF to PE. Such a relation would predict a transfer of 15.9 nC between PTFE and PE instead of the observed 13.7 nC. Of course the prediction would not be expected to be perfect as even for the standard electrode potential care must be taken in measurements as potentials are chemically pure can vary with ambient conditions such as concentration, temperature, and pressure. The authors do control for the contact area from one experiment to the next, but it is not clear how well other variables are controlled for or even how much variation there is in force from one contact to the next due to maintaining the contact area. It should also be noted that in the standard electrode potential measurement it is the potential that is being measured, which could prove much more reliable than the charge transfer which could depend on many factors, including discharge and effective capacitance. Still, the difference between the charge transfers between the sum of charge transfers between PE and PTFE to PVDF and when the PE contacts the PTFE directly either provides reason to doubt that any quantitative information from this experiment (and only conclusions based on polarity are valid) or that a simple model of electron transfer based on relative energy does not adequately explain the observations presented. The repeatability of the charge measurement in a given sample pair from one contact to the next would suggest the transfer is highly reliable, and thus the model might be off, but without knowing if the charge transfer has this same level of repeatability when the experiment is repeated with two new samples of the same type of material. This reasoning applies to any set of three polymers, however it is additionally worth taking into account the actual chemistry of the PVDF which is a combination of the PE and PTFE. At first glance it might appear that the PVDF, having half C-H groups and half C-F groups, should transfer the same amount of charge, but in opposite directions, to the PE and PTFE. However, both when looking at the interaction with the metal and with the polymer-polymer experiments it is clear that the charge exchange between PE and PVDF (or the difference in their exchange in the case of the polymer-metal experiment) is about 50% greater in the polymer-polymer case and about 75% greater in the polymer-metal case than the equivalent exchanges with PTFE and PVDF. However, this simple view ignores the interaction between the C-H groups and the C-F groups which could interfere with the charge transfer mechanism. The authors argue that the PE has higher electron cloud range than the PTFE, this would be inconsistent with the observed charging as you would then expect the C-H bonds to have more of an effect on the charging than the C-F bonds, but instead the PVDF charging seems more similar to the PTFE charging which has only the

C-F groups. It is still possible the author's model is correct, and perhaps the stronger electronegativity of the F compensates for the larger clouds. Still, in the author's model it would then be reasonable to expect that the C-H groups which are next to the C-F groups would interact with each other the same way they would interact with the opposite group bound to a different sample in the experiment. That is, if the electron cloud mechanism is indeed what drives contact electrification, and the clouds in the experiment only depend on the difference between H and F since the C backbone is the same, then one would also expect internal contact electrification between C-H and C-F groups in the PVDF. If this occurs then the ability to exchange charge should be dramatically reduced, as many, if not all, C-H and C-F groups should be in close enough proximity with one of the opposite groups to allow for this internal charge transfer. Once the internal charge transfer has taken place neither group should be able to partake in charge exchange with PE or PTFE as the H would have already donated their available electron and the F would already have acquired an additional electron. The results presented suggest this does not happen and while PDFE charges less with PE or PTFE than the two do with each other, the charging does not seem to be close to zero from the uncertainties provided. On a related note FEP exhibits interesting charging behavior when contacting other polymers that is not immediately obvious within the author's model. FEP, which has the same C-F bonds as PTFE but with an additional C-C-F_3 on some functional groups, exchanges the same amount of charge between PE and PVDF within 5%, despite half of their functional groups being different. This could make sense in the authors's model if the C-C-F_3 group was able to accept electrons with approximately equal efficiency between C-H and C-F groups. However, the charge transfer between FEP and PVDF is just over 50% larger than the transfer between FEP and PTFE, despite having the same difference in number of C-F groups as between PE and PVDF. These results do not seem consistent with a model where charge exchange is simply based on the ability of functional groups to transfer and receive electrons based on the electron energy levels in those groups, however the authors point out there is contamination in the XPS data, so it is possible if the experiment is repeated in a cleaner set up the results could become consistent with the proposed mechanism. The remaining materials in the paper did follow a transitive trend, such that it would be consistent with models in which triboelectric series can be produced, as opposed to having charge polarity transfer where samples follow a permutation (A positive to B, B positive to C, C positive to A), but beyond that we do not discuss them further here as the complex and significantly varying functional groups makes it hard to make any quantitative conclusions. The authors additionally run experiments with the polymers and liquids, which we do not address as we are only investigating interactions where two solids are involved. The results of this experiment might be of interest to the reader independent of the theory proposed in the paper.

R. Elsdon and F.R.G. Mitchell published a study in 1976 that investigated charge exchange during sliding and rolling contacts, and importantly investigated the discharge that occurred at various pressures [56]. The experiment investigates the effect of several parameters on contact charging, but the reason to include it here is the observed effect of pressure, which does not depend on the cleanliness of the system or materials, or on the nature of the contact. The authors find that pressure in a vacuum chamber in which the experiment is conducted does have an effect on the charge transfer. The charge transfer goes down with decreasing pressure until hitting a minimum and then jumping up around 1 torr and stabilizing under 10^{-2} torr. They report this trend is consistent with discharge predicted by the Paschen curve, and any experiment on contact electrification needs to control or account for this effect, including being mindful of discharge changing preferred targets depending on distances between them at various pressures. Related to the measured charge at a given pressure after contact, the charge dissipation is also measured as a function of time. The dissipation rate followed a trend such that one over the charge density, σ, was proportional to the time, t: $\frac{1}{\sigma} \propto t$. We don't make any claims as to the authors explanation to the rate, but do think the results are worthy of attention, both because of the of the unique function of time, but also because although$\frac{1}{\sigma} \propto t$ the slope varies from one run to the next but is not dependent on the material. The authors do present an explanation for the trend, but it seems worth further investigation as to why the dissipation trend might vary and if it is related to the actual charging mechanism, or if it is independent as per Postulate 5.1. The authors also use various metals of different work functions in their experiments and while the Au, Ag, Ni, and Sn were films on brass spheres and the Al was hollow so only the brass sphere and stainless steel sphere were truly comparable, it still true that there is no obvious effect (statistical significance is not reported) of a given surface metal's work function on the charge transfer which should be taken into account in any proposed theory. The paper also covers experiments on the effect of force and time, but we do not comment on them here as the force experiment is only reported for one pair of materials and the time in contact is varied by changing the rub speed in the other experiment so there are too many variables unaccounted for and not enough repeatable data to make any strong conclusions from these last two factors. Still the discharge and decay data presented in this paper is significant and the effect of discharge on measured charge (including discharge to measurement devices) needs to be accounted for in contact charging experiments if any quantitative theories are to be developed.

An experiment by J. Lowell and A.R. Akande is worth mentioning in which they investigate variations in transferred charge between conductors and insulators [57]. Although this is an experiment between conductors and insulators as opposed to the insulator-insulator charge exchange that is the focus of our writing, their results on the variability of charge could still be useful to guide and caution experiments for all contact charging experiments involving insulators. For the metals in the experiment the authors use Au, Pt, Al, and Mg and the insulators in the experiment are polymers including PTFE, PVC, PMMA, Nylon, PC, PVA, and PS among others. Each metal-insulator pair was contacted 400 times in a vacuum with pressure under 10^{-4} Torr and the average charge transfer and the standard deviation were reported. The standard deviation was reliably at least 10% of the mean charge transfer for all pairs, with many pairs having significantly larger deviations to the point that their standard deviation is larger than the average transfer. This suggests there could be polarity flips and indeed the authors present histograms showing that while material pairs such as PTFE and Pt would always charge with a given polarity, many materials would have a small number of contacts where the polarity was opposite of the mean transfer. In an attempt to control for any variation of the sample surface from one location to the next causing variations in the charging behavior the authors also ran an experiment where they would contact gold against a sample at 400 different locations, then neutralize the charge with ionized nitrogen, and then contact the same locations 24 hours later. They then report a correlation coefficient for each sample, given by $C = \sum_{n=1}^{400} q_n q_n' / \sqrt{\sum q_n^2 \sum q_n'^2}$ with the index referring to each contact position and q_n and q_n' referring to the measured charge during the first experiment and after the repeated contact, respectively. The largest reported correlation coefficients was 0.91, but the in 12 of the 16 experiments the coefficient was under 0.8 with the lowest -0.01. It should be noted that the way the experiment is conducted a given metal sample makes repeated contacts at different locations on the insulator, such that there may be material transfer from the insulator to the metal on the first contact which then affects the charge transfer when that same metal contacts a new spot on the insulator. This might be responsible for some of the variation in charge transfer, but as many contact electrification experiments involve repeated contacts the results of this experiment are relevant to others that share this practice. This paper emphasizes the possibility highly variable charge transfer even in relatively clean and controlled experiments indicating an investigator hoping to develop a quantitative theory of contact electrification needs to consider how to control these variations. Additionally, care should be taken when analyzing the results of metal-insulator experiments when the contact to contact variation is not addressed.

5.3 Highly Cited Theories

In this section we will cover recently highly cited theories, and address at a surface level any issues with the experiments or derivations that lead to the theory.

The highly cited theories include multiple charge carriers and mechanisms. Wang and Wang argue that contact electrification is mediated by electrons and can be explained with energy band diagrams for materials with well specified band structure [32]. They further claim that for materials without a well specified band structure the charge transfer is due to overlapping electron clouds.

Wang and Wang [32] have a highly cited review from 2019 in which they claim they can narrow down the charge transfer in contact electrification to electron transfer between the materials involved. They use evidence of experiments which they break down into two classes- experiments between dielectrics (insulators) and other dielectrics, and experiments between dielectrics and metals. Within the dielectric and metal category the authors will claim that the charge transfer can be explained using an energy band diagram for the dielectric and the Fermi level of the metal. They use evidence of several experiments involving kelvin probe microscopy and one of an atomic force microscope. One experiment uses a platinum Atomic Force Microscope tip scanned on a parylene film with an applied bias and then characterizes the surface charge density with a scanning Kelvin potential microscope [58]. While this paper does show that the net charge transfer between the platinum tip and the substrate changes with changing relative bias, it should be noted that it is not shown whether the fundamental charge mechanism is being altered or if now there is simply an additional charge transfer mechanism that can complement, cancel, or overpower the unbiased charging mechanism. Interestingly, the review also cites an experiment where a Platinum/ Iridium tip atomic force microscope probe with zero bias is used to contact ionomer-polymer blends separated into two categories- blends with mobile ions and blends without mobile ions [59]. A key result of this experiment is when the charge transfer is studied by scanning Kelvin probe the blends with mobile ions had a strong change in their surface potentials while the blends with no mobile ions did not. This could lead to an interpretation that ions are involved in the charge transfer process, but this is not mentioned in the review. The authors then go on to mention that there is a recent atomic force microscope study that supports metal-insulator contact electrification is due to electron transfer. The experiment demonstrates the ability to measure a constant current using a conductive-atomic-force-microscope with a platinum coated silicon probe on MoS_2 [60]. However, the article points out that the current is not observed when the sample is silver, p-type silicon, SiO_2, or what they describe as ”traditional TENG polymer samples”. The authors of the review do not address why this behavior should be expected if contact electrification between a metal and an insulator is normally an electron mediated interaction. In addition to any concerns with the evidence from the papers they cite, they also fail to articulate how the results they summarize would lead to the conclusion that the charge carriers are electrons. They claim it can be shown that there is charge transfer which depends on the time in contact, as well as whether the contact is tapping or sliding, but do not put together the case for why this indicates electrons over ions or material transfer. They attribute a limit on the maximum charge that can be transferred to the dielectric breakdown of air. It is clear that the impact of discharge can play a roll in the maximum charge transfer between two surfaces, but they do not address what they expect the limit to be based on their cited experiments materials and geometry nor do they consider the equilibrium effects between the mechanism driving charge transfer and any discharge that might be occurring. It is known that the ability for atmosphere or another gas to mediate discharge via breakdown follows a Paschen curve such that any given pressure has a minimum voltage required for breakdown [56], but it is not addressed how knowing the nature of the breakdown can be turned into evidence for one charge carrier over another. They then jump to the previously mentioned conclusion that the charge transfer can be explained with the energy band diagrams despite using assuming a temperature of 0K for this explanation which is contradictory to the cited experiments which are carried out with ambient temperatures as high as room temperature.

Wang and Wang then turn their attention to the dielectric-dielectric case. The authors cite several articles claiming that they show that contact electrification can be explained by surface states for insulators with well defined band structures. The first paper mentioned is written by G.S.P. Castle and L.B. Schlein and attempts to explain charge exchange using a model based on data from toner-carrier charge exchange [61]. The paper presents a model where charge transfer can be predicted based on the diameter of the toner-carrier particles, and when comparing their model to experiment it should be noted they only mention the data comes from a variety of materials without specifying what they are. This is already an issue and many papers present data indicating the materials involved in contact electrification play a dominant role, not just geometry (indeed geometry is often left out of the discussion and often materials used have similar or symmetric geometries). Further, this paper when comparing their theory to actual experiment they first change their calculation to a limit where their predicted quantity (which was originally a relation between charge to mass ratio of charged particles and their concentration in the mixture) ends up only depending on particle density and radius, completely neglecting the density of surface states at the core of their argument. Then when comparing to actual data from other experiments the data does not line up with their prediction well, and even when they say that an experiment is close to their prediction if it is within a factor of 2 in either direction there are still a substantial number of outliers. So even with their limiting case that drops the density of charge states on the surface of a particle and end up with a relationship with density and radius of the particles (which if accurate is still entirely possible, perhaps even likely, that it could be better explained through arguments focusing on physical parameters related to density and radius) the actual match between their calculation and the experiments they reference are not well matched, and thus should not be used to provide evidence that contact electrification can be explained by surface states as Wang and Wang do. The next two papers Wang and Wang turn to are a review by G.S.P. Castle that as far as of surface states simply references and summarizes this original paper Castle and Schlein paper with no further evidence [62] and a precursor paper by L.B. Schlein, LaHa, Novotny which has the same calculation used to compare with experiment and a similar level of significant disagreement with their referenced experimental results [63].

The next work Wang and Wang reference in making the case for electrons being the charge carriers in contact electrification is by Xu, Zi, A.C. Wang, Zou, Dai, He, P. Wang, Y. Wang, Feng, Li, and Z. L. Wang in which the authors experiment with post-contact charge dissipation at varying temperatures [64]. The experiments conducted by the group are stated to involve contact electrification between Ti and SiO_2 and between Ti and Al_2O_3, but it is worth noting the authors describe having an issue getting substantial charge in the Ti-SiO_2 pair so ended up first rubbing the SiO_2 with polyurethane to pre-charge the SiO_2. The Ti-SiO_2 pair are then heated to various temperatures between 353 and 583 K and the short-circuit charge is measured between the Ti and an Au coating on the back of the SiO_2.

The results of the experiment suggest that the residual charge on the material surface after contact does dissipate faster with increasing temperature, albeit in a highly non-linear way. Additionally, it should be noted that these experiments are conducted in atmosphere, so the effect of the local environment needs to be taken into account, and these experiments are solely on the dissipation of residual charge and do not track the rate of charge accumulation from contact electrification at the various temperatures. The authors attempt to explain the observed dissipation behavior by thermionic emission alone and use this to bolster their claim that the charge carriers responsible for contact electrification are electrons. There are two mistakes here and we will address both- the first is the interpretation that their dissipation behavior is well explained be thermionic emission, and the second is that even if the behavior were explained by thermionic emission that this would imply the carriers responsible for charge transfer are electrons. To properly determine if the charge dissipation data is well described by thermionic emission it is both important to determine the change in the rate of dissipation with temperature (if the exact rate cannot be determined, for example if it requires detailed of knowledge of a work function which can vary substantially based on surface conditions) and how other coactive dissipation mechanisms will vary with temperature so that the contribution due to thermionic emission can be isolated and analyzed. The authors do not address what coactive mechanisms might exist and the corresponding effects, other than the brief mention of the temperatures being above the boiling point of water (although relative humidity in the experiment is not zero), so any analysis done indirectly assumes thermionic emission is the only contributor to charge dissipation. The analysis of thermionic emission in the paper ends up using the equation for p-n junctions by Shockley [65] and used by Rhoderick to describe current flow across Schottky barriers in metal-semiconductor junctions [66], both of which require an applied voltage to be sensible, instead of the thermionic equation with an adjusted work function due to relative potential as Kiziroglou, Li, Zhukov, P.A.J. de Groot, and C.H. de Groot did [67], which would be the correct adjustment to make if they want to account for the relative bias due to the excess electrons on the material surface. This mistake leads to an error where their equation would lead to the belief that the thermionic emission should be proportional to the temperature, T, for a given surface charge, as opposed to the equation believed to be applicable to emission out of material rather than across a junction which indicates that the dissipation should be proportional to $T^2e^{\frac{-W}{kT}}$ for a given surface charge. This prevented them from correctly analyzing their results to determine if thermionic emission matched the charge dissipation (in fact the way the used their equation would imply that no electrons could exit the material at any temperature once the transferred charge had dissipated, without any justification as to why these electrons were different from others in the material). Now it is worth pointing out that even if the incorrect use of a modified thermionic equation involved in semiconductor junctions had not rendered their analysis invalid and had any conflating factors been controlled for, a confirmed observation of a material exhibiting thermionic emission after contact electrification is not alone evidence for electrons being the charge carriers as stated in Postulate 5.1.

Wang and Wang then attempt to explain contact electrification involving materials where the electronic structure is not well defined, such as is the case with polymers or organic materials, and put forward a theory that in such situations contact electrification due to overlapping electron clouds. The argument relies almost entirely on earlier work of Z.L. Wang in which an experiment by Li, Zhou, Zi, Zhang and Z.L. Wang is conducted with KPFM (Kelvin probe force microscopy) demonstrates that when the platinum-coated silicon KPFM probe is used to charge SiO_2 or parylene C there is a correlation between charge transfer and a the phase shift, ϕ between the reference signal and the cantilever deflection signal, particularly around the point where the change in the phase shift, $\Delta\phi$, changes sign [68]. Wang and Wang argue that this experiment proves that charge transfer occurs only when there is a repulsive force between the probe and the sample, and the point where the force switches from attractive to repulsive can be interpreted as the point where electron clouds begin to overlap. They make the case that this suggests electron cloud overlap is required for charge transfer and thus the mechanism of charge transfer is electron movement from a molecule in one material to a molecule in the other, which is enabled only when the electron clouds overlap, so evidently the charge carriers are electrons. The issue with the final conclusion, that there are electrons moving from one molecule to another, is the interpretation that contact would only be required for electron transfer. The materials involved in contact electrification start off at lower net charge than after the charge transfer so it should be understood that the charge transfer we are interested in cannot be driven long range electric fields, thus either at very close distances electronic properties of the bulks or surfaces must interact with each other in someway to create a strong electric field to move the charge carriers, or else actual contact is required to generate forces or allow chemical interactions that would move electrons or cause ions to become more strongly bonded with the opposite material. In fact the authors even go as far as using atoms in opposite materials forming bonds with each other (either ionic or covalent) as part of their description of how charge transfer occurs, but the formation of such bonds would also allow for and explain ion transfer where an ion becomes more strongly attached to the new material than its original host and thus stays with the new material when contact is broken and is thus responsible for the charge transfer. With this in mind it should be understood that the cited experiment does not provide evidence for either charge carrier over the other.

Wang and Wang proceed to turn their attention back to experiments on temperature dependence of contact electrification. The reference the work of Shiquan Lin, Liang Xu, Cheng Xu, Xiangyu Chen, Aurelia C. Wang, Binbin Zhang, Pei Lin, Ya Yang, Huabo Zhao, and Zhong Lin Wang where an Au coated silicon AFM tip is contacted against various materials including SiO_2, Si_3N_4, Al_2O_3, and AlN (Aluminum Nitride) with the ability to heat the tip and contacted sample independently [69]. The experiments are conducted in Argon at atmospheric pressure, with the AFM in peakforce tapping mode to reduce rubbing between the tip and the sample. The first results presented demonstrate that for the SiO_2 sample, when the tip and sample are maintained at the same temperature, increasing the temperature of the materials results in both decreased charge transfer and more rapid dissipation of that transferred charge. This on its own is not that interesting, we have discussed temperature dependence of charge dissipation above and it is unsurprising that the measured charge transfer would be reduced with increased rates of charge dissipation. In the paper it seems as if the experiment is run just one time for each sample with a given set of parameters, and the fact that they are using the AFM to transfer charge many times across the surface and then measure the charge using Kelvin probe force microscopy (KPFM) also many times across the surface to justify lack of multiple samples. Based on many other experiments related to contact electrification discussed above and in the following section on highly cited experiments, it should be clear that these experiments need to be repeated many times with different samples of a given material to ensure repeatability, which most experiments lack. However, if the experiments do prove to be reproducible the results here show a trend worth understanding as it could have substantial impact on interpreting other contact electrification experiments. The trend is that for all four materials used in the experiment, when the sample is held at a fixed temperature of $313K$ and only the tip temperature was allowed to vary, then the charge transfer was approximately linearly related to the temperature of the tip. This polarity was such that the higher the tip temperature the more negatively charged the sample became, and importantly this was *independent of the initial polarity* when the tip and and sample temperature were the same. It is important to note that this is a conductor-insulator contact, not the insulator-insulator interaction which we are calling contact electrification. Thus, it is important to understand if the trend observed here can be explained by the properties of the conductor alone, in which case it is important to account for this in any other experiments that attempt to investigate contact electrification between insulators using a conductor-insulator experiment as a proxy, or if it does actually reveal something about how the insulator is being charged in which case it could reveal information about the mechanism behind charge transfer in contact electrification between insulators. That is to say Postulate 5.2 prevents any conclusion about the nature of charge transfer between insulators to be drawn from an experiment between an insulator and a conductor when the charge transfer can be predicted from the properties of the conductor alone or when the conductor has properties that enable charge transfer that an insulator is not known to have. The conducting tip of the AFM could be affected by temperature in one or more of several known ways which would not be related to contact electrification, but are simply the result of the tip being a conductor. Importantly, whether the charge transfer between the conducting tip and the insulating sample has a polarity such that the insulating sample charges negatively or the opposite, temperature effects that affect charging only because the tip happens to be a conductor can still result in the increase in negative charge transfer to the insulator including a possible polarity flip from a positive charge transfer to a negative- simply as the result of more free electrons existing at the surface of the conducting tip. The first of these would be true thermionic emission- a conductor heated to high enough temperature will emit electrons which could charge a nearby insulator, but could not be used to draw conclusions about the charge carrier responsible for contact electrification between that insulator and others. If this were the source of charging via electrons the charge transfer might reasonably be expected to follow the thermionic current which related to temperature by $A \cdot T^2 e^{\frac{-W}{kT}}$ with $A = 100 \pm 4$ and $W = 4.25 \pm 0.02$ [70] , the results in this study do not seem appear to follow this fit (from the exponential component which does not match the linear nature of the data, independently of the exact coefficients) so thermionic emission can be ruled out as the dominating factor in determining charge transfer. Another known influence on the electronic behavior of conductors is the Seebeck effect, in which conductors with a temperature gradient will experience a current until equilibrium has been reached with a resulting voltage (and thus charge) gradient. Since the tip of the AFM is being heated there will be a temperature gradient between the tip and where the gold tip is grounded and thus the tip will not be at $0V$ relative to ground. The Seebeck coefficient for gold is $1.5\mu V/K$ and the temperature difference between the tip and standard room temperature varies from about 15 to 135 K depending on the temperature of the lab, resulting in 22.5 to 202.5 μV. The maximum voltage in the paper is in the range a few hundred mV so it doesn't appear that an equilibrium effect between the voltage at the tip due to the Seebeck effect and the insulator could be responsible for the charge transfer. The authors argue that the observed temperature dependence is due to change in electron energies as predicted by the Fermi-Dirac distribution

$$f(E) = \frac{1}{e^{\frac{E-E_f}{kT}} + 1}$$

which states that with increasing temperature there will be more electrons in higher energy states. Energies near the Fermi level, E_f, have much larger probabilities of being occupied than energies much higher, and as temperature increases these nearby energies have probabilities of being occupied that increase in a way roughly linearly proportional to temperature in the temperature range reported in the experiment. First, it is worth considering under which conditions this linearity would be expected, then we can focus on if those conditions are met then what else would be necessary for the observation to be consistent with an electron carrier model with transfer based on available surface states. The authors suggest that when the two materials come into contact the material with the higher energy electron will donate an electron to the other material provided there exists a state in that material for the electron to occupy. Following the authors' convention let E_0 be the highest occupied surface state in the insulator. Then following the authors logic, if the metal has an electron with energy greater than E_0 it should donate an electron, and if the metal has only electrons with energy less than E_0 then it should accept an electron. Of course the Fermi-Dirac distribution suggests we cannot take such a simple approach, as at any temperature above absolute zero there is a finite probability of an electron having any energy, and even taking into account the finite number of free electrons in the metal there is still a large range of energies that have a reasonable chances of being occupied or unoccupied. A slightly modified approach might be to argue that if the probability of the metal having any state occupied that has energy greater than E_0 is larger than the probability of having any state less than E_0 then over the many contacts between the AFM tip and the insulator there should be a net transfer of electrons from the metal to the insulator. Further, the larger the ratios of these probabilities the larger the charge transfer should be. The exact calculation of probabilities should be achievable, but requires knowledge of the density of states in the gold tip. If the states are simply assumed to be a continuum then there are an infinite number of states arbitrarily close to any given energy, which in turn will have a finite probability of being occupied by the Fermi-Dirac distribution, and thus will always lead to the probability of at least one such state being occupied approaching unity (100 states each with 1% probability of being occupied gives a 37% chance none are occupied, increasing that just 10x to 1,000 such states give a probability of just 0.004% that none are occupied). Without calculating the density of states it is hard to make any strong statements about the charging versus temperature behavior we expect to see, but we can still make some broad observations. The first is that the linear behavior the probability distribution occurs for energies near the Fermi level, thus if E_0 is not close to the gold Fermi level we would not expect to see a linear change in charging behavior from the Fermi-Dirac distribution alone. The second is that the Fermi-Dirac distribution changes symmetrically with temperature about the Fermi level, that is if $E_0 = \mu - \delta$ then for any increase in occupancy probability for an energy state above μ there is an equal decrease in occupancy probability below μ such that the total probability between $\mu - \delta$ and $\mu + \delta$ does not change. This means that any change in the charge transfer would occur only from states with energy above $\mu + \delta$. Since the states further away from the Fermi level change less linearly with temperature this could put constraints on how far below μ E_0 can be and still maintain a roughly linear relationship. This also puts limits on cases where the charge transfer when tip and sample temperature are equal is of the polarity such that the tip is negatively charged, as this would require enough of a change in the Fermi-Dirac distribution that despite opening up even more sites below E_0 the higher energy states would be enough to compensate and surpass these vacancies. Despite these concerns, it is still possible that for an appropriate E_0 and μ the linear relation between temperature and charge transfer could be consistent with the authors' model. If this is the case, then this data could support a surface state model if it can be shown that the results are consistent with an insulator with some available surface states of high enough energy that at low tip temperature there are no electrons available to transfer and fill those states, but at higher temperature these electrons become available, and that the increase in temperature would not independently create an excess of electrons at the tip surface which could then transfer to the insulator sample independently of the electron energy and available surface states. Further, the experiment needs to be consistent with the observed reduction in charge transfer when the sample is also heated, and with the decay, again while not providing a separate route that excess electrons would have become available. The authors additionally run an important experiment where the tip has a voltage bias applied to it at various tip temperatures, and it should be possible to show whether these results are consistent or inconsistent with the surface state model and electrons being the sole charge carrier in contact electrification. The issue is this important experiment with the voltage bias between the tip and an SiO_2 sample is that the potential of an insulator is poorly defined. This means without backing the insulating sample with a conducting film or knowing the geometry of the chamber then it is impossible to determine if the change in charge transfer is simply a change in the amount of free charge on the AFM tip (and thus a change in the number of available electrons for charge transfer) and similarly it is a change in the electric field near the tip that would lead to a change electrons emitted or if there is actually something fundamental about the voltage bias leading to a change in the energies of electrons in the conductor that allows them or prevents them from jumping to the the insulating material and occupying surface states in specific energy ranges. Thus, despite the experiments with applied voltage bias affecting the charge transfer between the gold conducting tip and the SiO_2 $\sim$6x more than changing the temperature of the tip by over $100K$, no conclusions about the charge carrier involved in insulator-insulator contact electrification can be made from this portion of the experiment. Without a well defined voltage experiment or the temperature experiment repeated with two insulating materials it is impossible to make any conclusive statements about the nature of the charge carriers in contact electrification from these experiments as despite clearly showing a correlation between charge transfer and tip temperature when the sample temperature is held fixed, it is not possible to know if the reason for this is a change in the Fermi-Dirac distribution based on change in temperature and this resulting in a change in the number of electrons with high enough energy to occupy a surface state in the insulator as the authors suggest, or if it is simply changing the number of free electrons at the interface which then attach to the nearest surface which happens to be the insulating material, perhaps due to the same mechanism that causes more rapid charge dissipation when both tip and sample are heated. While this experiment lays the groundwork for interesting experiments on the effect of temperature in contact electrification between insulators, it should not be used as evidence for electrons being the charge carrier in such interactions as Wang and Wang have.

Wang and Wang then reference a study on contact electrification by Shiquan Lin, Liang

Xu, Laipan Zhu, Xiangyu Chen, and Zhong Lin Wang where the effect of illuminating materials on charge dissipation after contact electrification is investigated [71]. Their experiments involve charging SiO_2, PVC, and PMMA with a gold coated silicon tip and then exposing the charged sample with ultraviolet (UV) light of various wavelengths and then measuring the charge dissipation. There are two main issues, one with the experiment and the other with their conclusion. The issue with the experiment is they do not control and measure any possible electron emission before contact charging in order to show that the charge dissipation they measure is not simply the removal of the electrons native to the sample, rather than being a unique signature that electrons had been the charge carrier during the contact electrification and were distinguishable from the control emissions. That is, the authors have only run an experiment on charge dissipation and Postulate 5.1 prevents any conclusions about the nature of the charge carriers from being drawn from such experiments. The issue with the conclusion is that their results actually showed that for both negatively charged samples (SiO_2 and PVC) and positively charged samples (PMMA) illumination with UV light dramatically accelerated charge dissipation, yet the authors still concluded that these results support the hypothesis that electrons are the charge carriers in contact electrification. Even if the experiment had been properly controlled by observing the effect of UV exposure prior to charge transfer, the fact that the positively charged sample also discharged under appropriate radiation cannot be explained by emission of electrons (as this would have led to a larger measured positive charge, not a reduced one) means that the two other samples cannot be used to support the electron carrier theory and invalidates their conclusion. This applies to this individual paper's conclusion, but also cannot be used as evidence in general for the electron carrier hypothesis as Wang and Wang do in this review.

The preceding papers make up the entirety of the evidence for Wang and Wang's case for electrons being the dominant or possibly sole charge carrier involved in contact electrification. While we make no claims related to any additional data the authors of the various studies might have, or unpublished calculations of Wang and Wang that might provide a complete argument, it should be clear from the discussion above that the data published in these papers does not constitute a conclusive case for electrons being the charge carrier, or even for electrons definitely being at least partial contributors. Despite the reviews high citation numbers at the time of writing, the arguments presented within it should not be accepted as complete or conclusive and thus its primary conclusion must be considered invalid based solely on the information contained within.

A highly cited theory that focuses on polymer-polymer contact electrification put forth by C.B. Duke and T.J. Fabish argues that charge exchange is driven by the relative energy levels of donor and acceptor states in the materials involved and claim that this theory is backed up by their experimental investigations between polystyrene and copolymers of styrene and PMMA, including copolymers with carbon black [72]. The authors use an electron carrier model of contact electrification as indicated by their use of metal work functions and fermi levels , and their argument will rely on the transfer in metal-polymer contacts and polymer-polymer contacts being the same except for the difference between the metal donor spectrum and the polymer donor density of states. Their model for electron transfer from a metal to a polymer is simply the probability of polymer acceptor state being unoccupied multiplied by the density of acceptor states (which gives the probability of an electron transferring from the metal to the polymer) minus the probability of a donor state being occupied multiplied by the density of donor states (which gives the chance that an electron returns to the metal), integrated over the relevant energy range. The distribution of donor and acceptor states in the polymer are inferred by first assuming each of the two sets of states independently follow a gaussian distribution, then by contacting the polymer with a variety of metals with various work function and thus varying fermi levels and observing the direction and magnitude of charge transfer. They use this method on both PS and PMMA, the claim then a copolymer will have a density of states given by a linear superposition of the two individual density of states from each material, with the coefficient given by the mole fraction of each component. The authors attempt to create an experiment to confirm their density of states model, and choose to use a ”total blow-off measurement” where in tone and carrier particles are mixed together where they exchange charge and then the charge per unit mass of toner lost from the sample is measured and reported. Duke and Fabish acknowledge that this method is not very reliable quantitatively for various reasons including geometric variations between individual toner and carrier particles, material degradation, and interactions with the container walls. However, they claim that the method has reliable polarity measurements and that it should be able to quantitatively agree with their theory within an order of magnitude despite these challenges. The results of their experiments do indeed agree with the polarity predictions, the actual value of the charge transfer is off (as the authors predicted it would be due to non-repeatable aspects of the experiment) and there aren't enough repetitions or alternate measurements to show a real agreement between theory and experiment. Further, even the polarity predictions are based on just two polymers in mixed in different ratios with the addition of carbon black to contribute metallic properties to the material and the claim that the terpolymer coated metal polymers used in the experiment have the same electronic properties as 15/85 PS/PMMA, and an experiment using so few materials, mixed in only three ways is not enough to establish the trend lines which would be available if more data points were used and in turn would provide much more convincing data as a well matched slope could compensate for the substantial mismatch in the prediction of individual values. As published, the experiment does not provide adequate data to support the theory in a substantial way and the theory itself does not sufficiently address other common observations in contact electrification experiments such as large variations in charge transfer from one experiment to to another or the difficulty in establishing a clear order of materials from positively charging to negatively charging the way metals can be arranged by fermi levels. Thus this work alone should neither be taken as evidence that electrons are the charge carriers in contact electrification or that electronic states available in polymers determine the magnitude and direction of charge transfer.

On another side of the charge carrier debate a review by Fernando Galembeck, Thiago A. L. Burgo, Lia B. S. Balestrin, Rubia F. Gouveia, Cristiane A. Silva, and Andre Galembeck makes the case that ions are the charge carriers in contact electrification of polymers based on experiments that map the surface charge distribution after contact electrification [73]. The authors' argument relies on showing that material transfer occurs in contact electrification experiments and then being able to correlate the locations where material transfer has taken place with the locations where the sample has become charged with a given polarity. The claim that material transfer can occur we are in agreement with as discussed in Section 5.1 Key Experiments on and Related to Contact Electrification with the authors of this paper also referencing Baytekin [24] and Piperno [51]. The challenge is in the second step and showing not only that this material transfer can occur, but that the material transfer is actually responsible for the observed charge transfer, either in its entirety or for at least a portion (even with the possibility of accounting for charge transfer of opposite polarity as the net charging). The study which the review relies almost entirely on is by Burgo [74] and is discussed in Section 5.4 Highly Cited Experiments, where it is shown the experiments contained within fail to prove that material transfer and charge transfer follow same spacial distribution in the contacted materials. Without this key piece of evidence all the review is able to do is show that material transfer can occur between contacting polymers, which we do not dispute, but not that material transfer is actually responsible for contact electrification. The review also cites a paper by Lia Beraldo da Silveira Balestrin, Douglas Del Duque, Douglas Soares da Silva, and Fernando Galembeck, which contains an experiment with the contact charging executed identically to the Buro study. This further confirms material transfer in their experiments with PTFE and PE primarily via Energy Dispersive X-Ray Analysis (EDX) and Backscattered Electron Imaging (BEI) , but for the same reason where the samples are spun while in contact with each other for a large number of rotations, any correlation between the location of material transfer and the location of charge transfer cannot alone be used as evidence that the actual charge exchange in contact electrification is mediated by material transfer [75]. The review does not actually include identification of the charge carrier in its conclusion, but it should still be noted that their section on identifying the carrier relies entirely on these two papers as evidence of material transfer being responsible for contact electrification in their section on identifying the charge carrier, and as the experiments in both of these papers involve such a large amount of rotational rubbing to the point that correlation between the spacial distribution of material and charge transfer cannot be used to as evidence of the charge carrier involved, no conclusion should be made about the role, or lack there of, of material transfer in the phenomenon.

In 1951 Harper published experiments on contact electrification between dissimilar metals that he argues is consistent with the theory that the charge exchange in the metal-metal case is driven by equalization of the fermi levels in the two materials [45]. While this is not a theory for insulator-insulator contact electrification, it is worth discussing here as theories involving electron energy levels driving charge transfer between insulators can be based on or influenced by the belief that the theory of contact exchange between conductors is well understood and confirmed. Harper presents detailed calculations on what the expected charge transfer should be based on the difference in fermi-levels, showing that it should depend on the capacitance between the metals at the time that charge stops tunneling between them as they are separated. While the calculations are detailed, they end up requiring knowledge of this tunneling contact-distance and both this distance and the details of the capacitance depend on the surface structure at a level of detail that is not possible to measure. Thus, when comparing the theory to his experimental results there is a level of uncertainty that makes it difficult to determine if the observed charge transfer is actually consistent with the theory at a quantitative level. Further, the actual measurement of the charge transfer ends up being highly variable, and in the published results there are substantial differences between what they report as the measured ”uncorrected charge” and what they call the ”corrected charge” based on the change in charge when the metal sample in an experiment is removed from its mount. The metals used in the experiment were sometimes electroplated on a metal of another type, and Harper does address and recognize that there can be oxide films that form on the material surface and other variations in the surface structure that cannot be controlled for. The experimental results presented lie outside the range of values the theory would predict, which Harper attributes to the metal surfaces and the difficulty in measuring charge, and argues that the results confirm that charge exchange between metals is due to equalization of the fermi-levels. While there does seem to be a relation between relative measured contact potential of the metals and the charge exchange, the data presented in this paper does not appear to match the theory at a level of detail to claim the theory is quantitatively predictive. For this reason, while the theory is possibly correct, further experimental results are needed before it should be considered established that the theory quantitatively explains and predicts charge transfer between metals.

5.4 Highly Cited Experiments

The experiments contained in this section are highly cited and thus have influenced the trajectory of development in the field of contact electrification, but that we believe contain critical flaws or fail to control for key variables that makes drawing reliable conclusions from them impossible.

A highly cited paper by Thiago A. L. Burgo, Telma R. D. Ducati, Kelly R. Francisco, Karl J. Clinckspoor, Fernando Galembeck, and Sergio E. Galembeck, is an experiment where an attempt was made to compare the distribution of charge on polymer surfaces, including those of PTFE, PMMA, and polyethylene (PE), to the distribution of material transferred from one polymer to another [74]. The issue with the paper is not the concept of the experiment- it would indeed be enlightening to know that the physical location of material transferred either is or is not located at the same spots as transferred charge of a given polarity- it is that the experimental evidence to weak too draw a conclusion one way or another, and further the methods and results have certain characteristics that make their reliability questionable. First it is worth noting that in their experiments where a square sheet of a polymer is contacted by a disc of another polymer, the contact is not a simple tap or even a non-slip roll, but is a rubbing contact where the disc is spun at $5,000rpm$ while in contact with the square sheet at a pressure of $1.5 \pm 0.25kPa$ for 1 to $3s$. This means that the disc completes between 83 and 250 entire rotations during each experiment. In an experiment designed to spacially correlate material and charge transfer any rubbing at all is an immediate cause for concern, and intentionally spinning one material on the other for more than 83 complete rotations makes drawing any conclusions about a possible correlation completely impossible. The spinning process makes it impossible to distinguish between several different processes that can result in the same distribution: (1) the original contact transferred material and charge, locking them into place, and the following spinning had no affect on those original positions, (2) the original contact could have transferred charge such that the charge carriers are locked into place, then during spinning any original material transferred along with additional transfer during spinning is moved around until rotation stops and the material ends up in its final observed position, (3) The original contact transfers material, locking it in place, then during spinning any original transferred charge and any additional charge is moved around until rotation stops and the charge is in its final observed place (4) a combination of the proceeding where both charge and material can move during spinning or even a case where some material and charge is locked in place while some is free to move during spinning, (5) the original contact transfers both charge and material, however during spinning the material moves around and collects or deposits charge so that at the end the transferred material has a net charge, though it is not from the original transferred charge and this process might not even involve the original charge carrier, (6) there is a slight asymmetry in the contact between the disc and the square sheet, leading to more pressure on one side, in this area there is more material transfer and material from the disc begins to build up, then on the other side there is still contact, but lighter, in that area standard contact charging occurs with little or no material transfer, this means that the disc has acquired a net charge opposite that of the square sheet, this piece of disc then comes into contact with the patch of the same disc material that had been deposited onto the sheet, now since the materials are the same the charge will redistribute itself approximately evenly between the patch and the original disc, meaning the patch now has the same charge as the disc which is the opposite charge of the rest of the square sheet. Since the six processes laid out above could all occur in experiments where one sample is rubbed against the other while undergoing many rotations, even if the results seemed reliable, this methodology prevents the drawing of any reliable conclusions from the experiment. Some of these methods might be able to be ruled out or be more likely from some simple experiments or additional data not presented in this paper. For example, if bipolar charging in only two spatial regions (one positive and one negative) on one material, but on the material that spins against it the bipolar charging forms a chess board pattern then method (6) is less likely to explain the observed bipolar charging. However, if the second material also exhibits bipolar charging in just two spatial regions then this is more evidence supporting (though certainly not proving) that mechanism (6) could be the reason for the observed charge distribution. Thus, presenting more detailed data on the charge distribution of each individual pair could help to narrow down which of the above mechanisms is responsible for the charging behavior reported, which could in turn allow for a strong conclusion on possible charging mechanisms and lead to insights about the charge carriers involved. Another paper by Lia Beraldo da Silveira Balestrin, Douglas Del Duque, Douglas Soares da Silva, and Fernando Galembeck, which includes members of the same group, does have one figure indicating that PTFE rubbed with PE causes both materials develop the two region bipolar charging, but it is not clear this experiment is repeated enough times with the same results to draw any strong conclusions [75]. Independently of any issues with the methodology (or at least it seems at first), the results seem questionable for two main reasons. The first is that all the potential maps for PTFE and PE (which are the main results shown in both the primary paper and its supplement) show a bipolar map with one end positive and the other negative, but the strange part is the values seem to be all around the probe limits at $\pm 3,300V$. This is concerning because having almost the entire map where any potential exists provide readouts at the limit of the probe could suggest the probe is not working correctly, or if the probe is working as expected then this would suggest the accumulated charge is so large that it is creating a potential saturating the reading of the scopes which would in turn prevent an accurate analysis of the charge distribution (appearing almost completely binary where there should actually exist finer details in the distribution), and if the charge is truly generating a potential saturating the probe then it could point to an issue with the experiment where if a material is experience huge bipolar charging beyond the probe limits instead of building up smoothly the charge could be generated from a source unrelated to the contact charging. Based on the methodology where the sample undergoes 83 to 250 complete rotations the most reasonable interpretation is the probe is operating as intended, but the huge amount of rubbing has built up so much charge as to saturate the probe which both hides the detail of the overall bipolar charge distribution reported, but also would hide any smaller mosaic bipolar charging that exists and would be relevant to understanding the charge vs transferred material distribution. It is worth noting that there is a comparison of calculated charge on the PTFE surface with a measured charge in a Faraday cup, and they do align much better than would be expected if the probe were completely saturated (indeed the Faraday cup measurement actually shows reduced order of magnitude compared to the calculation, although with the bipolar charging it is harder to draw a strong conclusion about the reliability of the probe from this as opposed to if it were of a single polarity), however they only show one calculation so it is not clear if this always fits well, or if perhaps they used the one non-saturated sample. There is notably one exception to this for the PE - PTFE pair, where instead the potential seems to be bound by $\pm 1,500V$ which is in the probes range, but strangely this sample also seems to have a different, smaller, spacial scale than all other maps for the pair. This also happens to be the one map that is shown with a visible light image of the PTFE after rubbing, where discoloration of the sample is used as evidence of material transfer at the same location as the charge of positive polarity on the potential map. The authors do not perform any mathematical analysis to show the strength of this correlation for the displayed sample or for a larger collection of samples if the took the data more than once, and while the image does display discoloration in the same general third of the circular potential map as the region of positive polarity, neither the shape of the overall bounding region nor the individual discoloration spots match well with the potential map. For this pair the authors also claim to show the presence of C-H bonds in areas of positive potential and the presence of fluorine, oxygen, and carbon in regions with negative potential. Unfortunately, independently of the reliability of these methods, they do not shed any further light into how the charge and material would have ended up in the same spot because of the large number of rotations during the rubbing contact. Lastly the authors present data on charge removal by various liquids the combination of Postulate 5.1 and the rotations prevent conclusions from being drawn from any differences in charge removal between the liquids or asymmetry in charge removal between positive and negative charges. So while the concept of establishing a spacial correlation or lack their of between charge transfer and material transfer distributions could prove quite illuminating, this experiment does not provide the clear and reliable data necessary to make any such inferences.

D.K. Davies published a very highly cited (over 700 citations at the time of writing) experiment in 1969 that attempted to establish an effective work function for various polymers by contacting them with various metals, the author claims the experiment suceeded and argues this means the charge carrier involved in this experiment is electrons [76]. The experiment is run in a vacuum maintained near 1μ torr, and the samples were prepared by washing with IPA (isopropanol). The materials used in the experiment were the conductors Cd (cadmium), Au (gold), Zr (zirconium), Pt (platinum), and Al (aluminum), and the insulating polymers PVC, Polyimide, PC, PTFE, PET, PS, and Nylon 66. The metals are formed into a grounded wheel which is then rotated against the various polymers which are mounted on a second grounded wheel, such that each metal will contact all of the polymers, and a slow rotation is maintained with periodic charge measurements. It is worth noting that originally the author used a different cleaning procedure which had resulted large scatter in experimental results, and the authors attributed this to variations in the polymer samples due to the original cleaning procedure. There are several reasons the experimental results as presented should not be used as evidence that these polymers have an effective work function, or that electrons are the charge carriers in this experiment. One such reason is that in the experiment the same metal samples are used with all of the polymers, and that the polymers are recontacted throughout many rotations, this leads to a substantial possibility of material transfer and thus contamination, not only between the polymers and the metal, but also through a secondary transmission between one polymer and another with the metal acting as an intermediary. Further in the data presented where charge density is plotted against contact potential difference between the contacting metal and a gold reference electrode, we do not see five clear bands as we would expect if each metal had a constant and well defined work function. Thus, the observed variation, if it is not due to a measuring artifact, must be the result of either the surface of the metal changing (possibly through contamination) or an accumulation of charge on the metal which would affect the charge transfer when it is brought into contact with the next polymer. Additionally, after the papers publication the Terris experiment described in Additional Experiments demonstrated that a metal-polymer contact could results in bipolar charging, and that this charging was not repeatable, which suggests there could be bipolar charging in Davies' experiment, making it impossible to establish an effective work function from the net charge while also offering an explanation to why the charge density measurements varied so much [54]. It does seem promising at first that the polarity of the charge transfer seems to match with a work function model (that is a metals with a larger work function will lead to a positive surface charge on the polymer and metals with smaller work functions lead to a negative surface charge, which could indicate an effective polymer work function between these values) closer inspection leads to two sources of potential doubt. The first is that all the measured polymers were assigned effective work function values between the larger work function metals and the lower work function metals, meaning they all exhibited the same polarity of charge transfer for a given metal, meaning there is no evidence it is the metal work function determining the polarity rather than some other property, as opposed to if two different polymers charged oppositely when in contact with the same metal, with magnitude consistent with a work function picture (there is a possible exception to this in the presented data with the nlyon 66, but if true the nlyon charged the in the opposite direction with Al as to that predicted by the metals work function, so this exception would hurt not help the hypothesis if true). The second is that in the presented data for nylon 66 and PC, while there is a clear trend between the difference in contact potential and the measured charge density, there are individual points for both samples with potential differences as large as 0.3 eV where the relative charge density is opposite of what the change in potential would predict, and similarly points with indistinguishable potential differences with charge densities varying by a factor of 5 (40 nC/cm^2). These large variations and a lack of any polarity differences between the polymers casts doubts on the reliability of drawing conclusions about the mechanism behind charge transfer in these experiments. Independently of the results' reliability it is important to follow the authors refrain from drawing conclusions related to insulator-insulator contact charging from these metal-insulator experiments per Postulate 5.2.

An experiment by J. Lowell published in 1975 is worth mentioning here, for although the experiment is performed with a metal-metal contact as opposed to the insulator-insulator contact that were are interested in, it solidifies the groundwork laid by Harper [45], discussed in the highly cited theories section, for what might be believed to be expected in a contact electrification interaction where the charge exchange is driven by equalization of fermi levels which would be relevant to those putting forth theories of insulator contact charging driven by a similar energy equalization [77]. The experimental method is to contact a sphere of one conducting material against a plane of another, then to measure the The experiment is carried out in a manner that casts doubt on the reliability of the data, and the data and assumptions made are too weak to support the author's main claim which is the charge exchanged between two conducting materials is given by the equation $Q = C_{effective}V$ where V is the potential difference between work functions as measured using the Kelvin probe technique, in which a voltage is applied to one conductor until there is no current flow between the two samples when distance (and thus capacitance) between them is varied, and $C_{effective}$ is the capacitance between the conductors, but modified from the capacitance predicted for smooth surfaces to account for surface roughness. The experiment is performed in atmosphere which implies the surfaces of the samples are not perfectly clean, and while the author does heat the samples to 50^oC and shows that there is no change in observed behavior, this is far from showing the surfaces are free of contamination. Additionally, the materials reported in the experiment are actually coatings on steel (for the sphere) and on brass or copper discs (for the plane) coated with the reported material by chemical or electrolytic deposition which could add complexity to the understanding of the work function of the samples. It should also be noted that the author himself reported that originally the charge readings were highly variable and he found that this was dramatically reduced by simple electrostatic shielding, but any remaining leaks in the shielding could affect the data, further the authors reported it could not be determined why, for example, the variations in charging between Cr and Ni were much higher than other pairs, for both temperatures the experiment was performed at. Shifting focus to the main claim of the paper, that the charge transfer should be governed by the equation $Q = C_{effective}V$, the author argues that the surface roughness will result in a true capacitance that is within a factor of 5 of what the smooth capacitance would be, but based on the reported surface roughness in the paper this could be a factor as large as 15 before taking into account any flattening that could happen during contact that remains after separation, however even with just a factor of 5 this allows such a large range of measured charges to fit the theory that it becomes difficult to determine if the experimental results actually support the theory, it is only possible to tell if the results are in great disagreement. The combination of uncertainty in the numerical results of the experiment and the factor of five range in the predicted capacitance provides a reason to doubt the ability for the data presented in the paper to support the conclusion that charge transfer between conductors can be predicted by the $Q = C_{effective}V$ equation, and in turn this should not be used as a starting point to predict charge transfer between insulators in the case that charge transfer is driven by some manner of equalization of energy levels.

A highly cited paper by C. Liu and A.J. Bard attempts to identify the charge carrier that mediates contact electrification in insulators by probing chemical reactions with the materials before and after charging [78]. The authors investigate contact charging between the polymers PTFE and PMMA. The first chemical investigation was two part, after being charged by PMMA the PTFE was put in acidic solutions and any change in pH was observed, and then separately charged teflon was placed in an acidic D_2O solution and then the solution was then connected to a gas analyzer to look for a D_2 signature in the mass spectrum. They found that the pH of the solution did increase and the D_2 signature was observed which the authors took to mean that the H^+ and D^+ ions in the two experiments were taking electrons from the PTFE and they argue that this is evidence for electrons being the charge carrier involved. The next investigation is into the effect of submerging PTFE into a $CuSO_4$ solution and then using energy dispersive x-ray spectroscopy to check for reduced copper that would be deposited on the material surface. The results were uncharged PTFE did not show a Cu signature while the charged PTFE did, which again was presented as evidence for electrons acting as the charge carriers. The next experiment looked for a reaction reducing $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$ using voltammetry as the probe, where the voltammogram would display a drop in the current plateau when the reducing reaction had taken place. They found that the reaction did not take place when uncharged PTFE was placed in the solution, but $Fe(CN)_6^{4-}$ did appear when charged PTFE was submerged instead, and again this was presented as further evidence for electrons as the charge carrier. Lastly, the authors used electrochemiluminescence (ECL) in which luminescence occurs when the a chemical probe (in this case $Ru(bpy)_3^{2+}$ and $S_2O_8^{2-}$) is reduced allowing a series of reducing and oxidizing reactions to take place which ends with photon emission. Again when the charged PTFE was submerged in the solution luminescence was observed, while when the uncharged PTFE was placed in the same solution no luminescence was observed. Although the authors argue that each of these is evidence for electrons being the charge carrier in these contact electrification experiments. However, if the PTFE is negatively charged by accepting electrons, the electrons are still bound to its surface, even if weakly, so it would take some energy to remove them. Thus, whether the PTFE is negatively charged from accepting electrons, accepting negative ions, or donating positive ions, the net negative charge arises from excess electrons on the material in one form or another, and there is no reason to suspect that removing those electrons in a reducing reaction would be easier if the electron were the original charge carrier. This suggests that these experiments simply showed that it is easier to chemically discharge the PTFE when it starts negatively charged than it is to chemically charge PTFE which starts off neutral. This seems reasonable and is related to Postulate 5.1 which implies that these experiments on their own do not actually lead insight into the original charge carrier in the contact electrification, and have simply shown it is easier to remove electrons from a polymer with net negative charge than from the same polymer when it is neutral.

CHAPTER 6

Experimental Procedure

In this chapter we discuss the parameters we believe worthy of investigation and that could provide insight into the underlying mechanism behind contact electrification. We then cover the considerations that went into our experimental design before going into the details of the equipment used and our exact experimental procedure.

6.1 Parameters of Investigation

Given the current state of experimental knowledge it is beneficial to put forth a set of parameters and corresponding experiments that if investigated and their effects understood will lead to a complete theory of contact electrification. While many of the effects and corresponding experiments will rely on each other to make progress in understanding the nature of contact electrification (for example if temperature affects charge transfer but rubbing does not, then one mechanism might be likely where if both temperature and rubbing affect the charging behavior, then another mechanism might be responsible, thus both experiments are necessary before conclusions can be drawn), we will still briefly give an example of what the results of any given experiment could indicate.

Of particular importance is determining which part of the interacting materials contribute to charge transfer, that is to discover if contact electrification depends on the material's surface, the bulk material, or both. The reason this distinction is so crucial is because it affects the experimental design for all investigations into the phenomenon. If the effect is due to the surfaces of the materials then great care must be taken to understand how surface structure may deviate from the bulk and to understand the effects of the ambient atmosphere on it. For repeatability the surface preparation from one experiment to the next must be the same, and the actual surfaces used in each experiment need to be characterized unless the environment can be kept clean and constant at a level known not to influence the surface structure. On the other hand if contact electrification is only dependent on the bulk material then an experiment only needs to be designed to ensure excess contamination is kept from the material surface, but the exact state of the surface can be allowed to vary much more, while only taking into account variables such as contact area or changing temperature of materials due to friction between materials of significantly varying surface roughness. One parameter's whose effects could help discern the bulk versus surface contributions is surface preparation and intentional contamination. If applying a small amount of liquid to the surface crystal significantly impacts the charging behavior, especially if this occurs even for experiments conducted in vacuum, then this could indicate the exact state of the surface is the dominant factor influencing charge transfer. This type of behavior could lead to even further insight if it is known that the liquid affects surface reconstruction, or if the concentration of a solution affects surface reconstruction and this can be shown to be correlated with charging behavior. Although it wouldn't necessarily differentiate between the bulk and surface contributions, it would also be worth investigating whether the orientation of a single-crystal affects the charge transfer, crystals with significantly different band structure or surface states depending on the orientation could help identify if these properties play a significant roll or if the charging is dominated simply by the bulk chemistry of the material. Further, if rotating the crystal along the axis perpendicular to the plane in contact (such that the same crystal face is in contact) changes the charging behavior a theory would need to be developed where the relative rotation of the crystals can influence the mechanism that drives the transfer. In the same manner it could be fruitful to determine if polycrystals exhibit different charging behavior from single-crystals.

An extension of this is probing the effects of intentionally inserting a medium between the crystal surfaces, without the intent of changing the surface properties of the crystal. Without intentionally adding a medium at the contacting interface, it is possible that charge transfer takes place while there is still some gas or thin liquid layer between the surfaces, but the resulting effects can be difficult to probe. Instead it is possible to intentionally add a medium through which the charge transfer must occur as a parameter of an experimental investigation. One such possibility is to insert a conductor between the crystals, which can be grounded or floating. In the case of the floating conductor one would expect that if the charge transfer was electrons driven by a potential difference between the contacting materials, then the insertion of the conductor will have no effect and charging. This is in contrast to a material transfer or ion mediated mechanism, in which the conductor would prevent ion flow or which would could accept material transfer, but would not pass it on to the opposite crystal. The result where charge transfer in not affected is more immediately enlightening than the case where the charging behavior changes, as in the latter case an argument that the conductor altered characteristics of one or both of the material surfaces could be made and control experiments would need to be established, but either result could still provide crucial information into understanding contact electrification. Further, if contact electrification is electron mediated, but is limited by either donating or receiving states, a conductor between the materials should allow for each material to independently donate or receive as many electrons as there are states, especially if the the conductor is held at a potential between the states of the two materials (this could include the conductor being grounded in fortunate circumstances), which would then lead to an asymmetry between the charge removed from one crystal and added to the other. This signal would be a clear indicator both of electrons being the charge species, and of state availability driving the magnitude of charge transfer if it is seen across various crystal pairs and has the correct polarity. A similar experiment of potential interest is probing the effects of a liquid bridge connecting the two solids. The bridge might allow ions or loose material to transfer from on surface to the other, and using liquids with different ion concentrations, viscosities, pH, solubilities, or polar or non-polar properties, among others could provide key insights into the nature of contact electrification if the charge transfer still occurs between the materials via the bridge for certain liquid properties and not others. The need to control any alterations of the surface properties of the interacting materials still exists here, but certain results could still be highly illuminating.

It is worth understanding if the underlying mechanism behind contact electrification saturates or not, and if it is replenish-able. That is do crystals fatigue overtime, such that they can longer donate or receive charge? If they do fatigue it is important to identify if it is the crystal that donates charge or the crystal that receives charge that prevents infinite charge exchange, and if it is always of the same polarity. The actual value of the total transferred charge could provide additional insight into the charging mechanism. If a charge transfer stops after the number of transferred carriers is equal to an integer multiple of the number of lattice points in a crystal surface, or the number of lattice points associated with a particular element of the crystal, then this could indicate these points are responsible for the charge exchange. The comparison between any charge transfer saturation and key values is made stronger when carefully accounting for any additional knowledge of the transferred charge distribution including any bipolar charging. It is also worth isolating the contribution of discharges, that is identifying if saturation occurs both when discharges occur and when they are suppressed or directed away from the crystals (for example, to avoid replenishment of electrons). Further, it is important to understand if the charge transfer can be re-initiated after fatigue through some mechanism such as electron bombardment, forced electric discharge (through fields, photoelectric effect, etc.), cleaning the crystal surface, or cleaving the crystal, and again if both crystals require this treatment or just one.

Mobile charge can be moved by electric fields, thus understanding the effect of an applied electric field on contact electrification can provide information on charge mobility after transfer and help identify the underlying mechanism behind the phenomenon. For example, if bringing the two contacting materials close to each other creates an electric field due to a potential difference, which in turn drives charge transfer, then applying an external electric field should increase or decrease the charge transfer depending on if the field is aligned in the same direction or opposite direction of the original field. Further, the transfer should cease when the external field exactly cancels the original field, and should be able to reverse the charging direction if the applied field is much larger than the original field. This effect should be able to be isolated from an effect on the charge after transfer has occurred by running control experiments where the field is only applied after the materials have separated after their original contact, and comparing this to the case when the field is applied the entire time or only while the materials are in contact. The control here is not perfect, as the applied field could still lead to charge transfer during contact that is unrelated to the charging behavior under investigation, masking the original phenomenon with another. Thus a result where an electric field has no effect is more enlightening than a result where there is an effect, but precise quantitative data on the change in charging behavior with various pairs of crystals combined with other investigations could still provide insight into the charging mechanism in the future. This effect should be different than, for example, a situation where the charge transfer is driven by chemical reactions or material transfer where there isn't a dominate effect from an electric field.

While modifying the pressure an experiment is run at might be chosen in order to suppress discharge, the ultimate pressure and time under vacuum can have additional effects on the experiment that could be worth probing. When a vacuum chamber is exposed to ambient atmosphere any humidity in the environment will result in water being sorbed by the chamber surfaces including any materials inside the chamber. This leads to significantly longer pump down times before reaching ultimate pressure as the pump down rate becomes limited by the rate of water desorption from the various surfaces. This effect is noticeable both in the different pump down times after venting the vacuum chamber with dry nitrogen versus ambient atmosphere, and in the increasing pump down time with increased time the chamber exposed to ambient atmosphere. Without previous data, there is no reason to believe the materials in a contact electrification experiment are any more immune to water sorption than the chamber surfaces. This means using a residual gas analyzer (RGA) to observe water vapor leaving the chamber should be able to serve as a proxy for the amount of water molecules still bound to the samples in the experiment. Observing charging behavior in a range of desorption rates could shed light on the effect of water molecules on the contact electrification process, and any experiments where the amount of sorbed water can change either within a run or from one run to the next should take care to account for this factor if there is any correlated change in charging magnitude.

Allowing controlled variations in material temperature opens up another useful parameter space. As mentioned briefly at the beginning of this section the contribution of rubbing (discussed below) is hard to isolate as it is difficult to eliminate all rubbing down to the order of a few Angstroms and because rubbing will generate heat from friction between the two materials. This makes determining influences fundamental to the rubbing action as opposed to changes in temperature difficult. However, the experiment can be designed to either monitor the material temperature to observe temperature changes from frictional heating, or actively control the temperature of one of or both of the contacting samples. This control can range from cryogenic cooling to heating until limited by the material characteristics of the samples or limits due to the temperature rating of the various components comprising the experiment. As with any additional probe or apparatus, any secondary effects from adding them need to be considered, and this can vary widely, for example, from heating changing the compliance characteristics of any epoxies used to additional wiring changing the local capacitance of the system.

The most difficult parameter to control might also be the most influential- the exact nature of the contact between the materials. While certain aspects are simple enough to control, such as the net force or the time in contact, creating anything near an exactly repeatable contact is exceedingly difficult. Even for the easier parameters, the ranges in which they are easy to control are often not the most enlightening. It is easy to vary contact time from milliseconds to months, but it is hard to create a reliable contact at the femtosecond or nanosecond level where fundamental time constants of the charging mechanism might become apparent. This is equally applicable to force, where large net forces are easy to exert, but the difficulty in having aligned, atomically smooth surfaces can result in extremely large local pressures at the smallest controllable applied force. The speed of impact when the crystals contact and applied rub round out force and time of contact as the set of variables that should be explored within their reasonable ranges to understand their effect, if any, on the charge transfer. Intentional rub is easy to apply and can be executed over a range of speeds and acceleration profiles, however eliminating on the scale of the lattice spacing (on the order of 5 Angstroms) is nearly impossible, especially when the materials are macroscopic (as opposed to an AFM tip). For this reason it is impractical to make claims as to if rubbing or a non-zero normal force is required for charge exchange to take place, but if increased force or rubbing does affect the charge transfer then claims can be made about charge mobility and the exact relation between the variables and the transfer can lend insight into the requirements for charge to be able to move from one surface to the other. The final aspect of the contact is perhaps the most important, the alignment of the two materials. While a cylinder on cylinder or sphere on plane contact might give repeatable contact areas on larger scales, their curvature fundamentally means at the atomic scale they are not smooth, and the repeatable contact area relies on deformation of the surface, which could affect the charging behavior. Alternatively, having a plane on plane contact allows for atomically flat surfaces and deformation free contact, but this comes at the cost of requiring perfect alignment when the crystals are in contact. In practice the alignment can take form in two parts. The first is any manual alignment, pre-contact this could be optical or using some sort differential force sensing between different parts of the crystal. It could also be done while crystals are in contact outside of the actual experiment, for example crystals could be mounted vertically and have epoxy attaching them to their respective mounts cure while one rests on the other, using gravity to let one sample lie on the other bringing them into alignment, alignment could come again from force sensors, this time equalizing normal force between the crystals at various points, or a proxy could be used for alignment such as adhesion between the surfaces in atmosphere. The second form of alignment is any passive alignment that occurs as the crystals materials each other. That is, the sample mount can be designed with intentional compliance such that when the two materials come into contact they are able to pivot into better alignment due to any inequality between forces at various points along the surface. Even without intentional compliance, there is likely to exist some ability for the materials to adjust their alignment upon contact when the relevant scales are on the order of tens of Angstroms. The trade off of increased passive alignment is reduced repeatability in the exact contact from one contact to the next. That is the exact way that the sample pivots can change from contact to contact, and during this process the edge of one surface will rub along the face of the other, possibly leading to unwanted affects and adding uncontrolled variations to the experiment. It is possible that the alignment is the dominating factor preventing qualitatively repeatably results from being obtained in contact electrification experiments as small changes in the alignment before contact and any passive alignment during contact can dramatically change both the actual area in contact between the samples and the nature of the nature of the contact via unintentional rubbing between one samples edge and the others face. Thus, the decisions of sample geometry and alignment techniques as well as determining the compliance the system will have can be critical to obtaining useful results from an experiment.

For all parameters of interest it is further worth investigating if there is any combination which leads to charge transfer when the two samples consist of the same material. If there is any charge transfer between like materials it is critical to understand if the mechanism driving the charge exchange is unique to the situation of self-charging or if it also exists when the materials are dissimilar. If the specific charging mechanism is unique to charge exchange between samples of the same material then it does not need to be accounted for in a general theory of contact electrification, for example if it were due to cold welding followed by material fracture. However, if self-charging is driven by a mechanism that can also drive charge exchange between dissimilar materials then the magnitude of self-charging becomes an uncertainty or correction factor in the experiments with dissimilar materials. That is, if the charging between like-materials can be is repeatable or can be controlled (for example if it occurs due to a known and consistent asymmetric contact) then this transfer can just be subtracted from the dissimilar experiments, but if the self-charging appears random and the driving mechanism cannot be suppressed, then this random charge transfer may occur at the same magnitude in the dissimilar experiments and thus becomes a minimum uncertainty that exists. Thus, if the self-charging magnitude is comparable to the magnitude of charge transfer between dissimilar experiments it will prevent a quantitative theory of contact electrification from being established until the self-charging can be controlled as the charging in dissimilar experiments will be able to vary wildly and possible even display polarity reversals from one contact to the next or from one experiment to another.

6.2 Considerations For Our Experiment

When designing our experiment our goal was to investigate a subset of the parameters, discussed in the Parameters of Investigation section, that would be likely to provide insight into the underlying mechanism behind contact electrification, while making sure that both building and running the experiment would be time-efficient and financially viable. With these constraints it is not possible to investigate all possible parameters and decisions have to be made not only on which parameters to investigate, but the best method for the investigation. For example, it might be possible to maintain a cleaner surface in ultra high vacuum, but you can run experiments much more rapidly in ambient atmosphere as the investigator does not need to wait for the system to pump down after setting up each experiment. In practice there must be a balance between speed and control of the experimental environment, and this optimization between speed and ideal conditions is mimicked throughout the experimental design process in balancing conditions and methods that might be ideal for one aspect of contact electrification with conditions that might be ideal for another. In this section we discuss the considerations that guided our experimental design.

Since financial considerations can affect every aspect of an experiment's design, a large influence was that Adam Collins had already been running contact electrification experiments in our group, which were focused on using single-crystals as the contacting materials as opposed to polymers or polycrystals, and on monitoring x-ray pulses caused by discharge between the crystals [6]. For his experiments he used an actuator to contact the two single-crystals, measured the normal force on one crystal and the position of the other, and used an x-ray sensor to monitor for electric discharge. The environment was controlled by building the experiment in a vacuum chamber, which could be evacuated to the 10^{-3} Torr range using a turbomolecular pump combined with a roughing pump. When designing our experiment, if any of these components could be used instead of needing to purchase new parts for a design that might be more ideal, we would use them if the detriment to the experiment was small enough.

An important consideration for our design was experimental repeatability. If the magnitude and polarity of charge transfer between a set of material samples varied from one to the next in our experiments, or if another lab would not be able to quantitatively repeat our results, then it would make interpreting our results and establishing a quantitative theory of contact electrification impossible. This naturally leads towards to routes of experimental investigation, similar to investigating the outcome of rolling a die. In the first route the investigator carefully and rigorously control all relevant aspects of the experiment. For the die this could include using dice with the exact same weight and surface characteristics, maintaining consistent landing surfaces, repeating the exact same starting position and the same forces driving the roll, and maintaining the exact same air patterns throughout the trajectory of the die. For our experiment this would include running experiments with the exact same bulk materials, maintaining the same surfaces including any reconstructions which would require identical ambient conditions and starting with atomically identical surfaces (requiring the use of single-crystals), ensuring the contacts are exactly the same between one run and another including both the force as a function of time and the geometry of the contact, and requiring identical sample preparation and storage or cleaving and treating the material in-situ if it is known this will create identical surfaces, among other controls. An alternate route is to design an experiment that is not as carefully controlled, but to repeat it enough times that the outcome can be investigated statistically and then develop a theory consistent with these results. For a die this could involve still maintaining as much consistency as possible, for example rolling the die on the same surface, dropping the die from the same height each time, and noting its approximate starting orientation, but then repeat the experiment many times and then statistically analyze the outcomes and create a theory consistent with the distribution of outcomes. For our experiment this would be attempting to keep each run consistent with the last, but repeating the experiment a large number of times and intentionally changing variables that we don't have exact control over (such as the exact nature of the contact) to see if there are consistent patterns in the distribution of charge transfer over many repetitions. Our experiment was designed following the second route, that we would run enough experiments under the conditions that we could control, that we (or another lab) would be able to observe the same results in terms of statistical distributions. That is, we might never see the exact same magnitude of charge transfer, but the magnitude of transfer across many repetitions would be consistent for anyone repeating the experiment.

In order to run the experiment many times, following our method of analyzing the statistical results over strict control of all possible contributing conditions that was not obviously achievable, we had to make key decisions on balancing speed versus consistency when they were not simultaneously attainable. The first set of decisions with this regard were on the atmosphere the experiment would be run in. A proper bake-out of the chamber and then allowing a turbomolecular pump to bring down the pressure to near the lowest final pressure would have both required between hours and days for each pump-down and experimental run, and subjected the equipment in the chamber to temperatures they are not rated to, requiring the purchase of new actuators and sensors and developing a mounting system capable of withstanding the high temperatures. For this reason we chose to run experiments at a pressure not higher than 10^{-3} Torr in order to suppress electric discharge (as any discharges not quantitatively accounted for would affect our interpretation of the amount of charge transferred between the materials), but which is not low enough we would consider the system clean and such that we believe at these pressures the ambient gasses can still affect the material surface. There was also no minimum pressure set and the pressure would decrease as the experiment was run, as we were only looking for the discharge suppression and not making claims about consistency of the ambient conditions which would have taken substantially more time and equipment to maintain. Since we already had the turbomolecular pump readily available, it was used in our experiments to expedite the pump-down time, rather than for any requirements regarding the ultimate pressure. Another design decision to increase the speed of pump-downs was to fill the chamber with nitrogen after each experimental run. We found using the boil off from the gas-use valve of a liquid nitrogen dewar was able to substantially reduce pump-down times when compared to venting the chamber directly to the ambient atmosphere in the lab. While the nitrogen was kept flowing at all times the chamber was not under vacuum, this too leads to increased variability in conditions from one run to the next, as runs where no re-alignment between the crystals took place were exposed to substantially less ambient atmosphere than runs with a re-alignment, and both of these had significantly less exposure to ambient atmosphere than the first run of each experiment where the chamber needed to be open during the entire process of mounting the crystal in the vacuum chamber. The desire to run experiments reasonably quickly also influenced our alignment procedure. Instead of designing the experiment in a way where microscopes or lasers would be inserted into the chamber for better alignment, or creating an algorithm to optimize alignment based on repeated series of charge transfer measurements and fine alignment adjustments, the experiment was designed to be aligned reasonably quickly by eye, and to have some compliance to allow the crystals to shift into better alignment during contact (we were unable to observe significant charge transfer using our alignment tools without this added compliance). This decision was not made only for the sake of speed, but efficiency was one of the contributing factors in choosing this method. The goal of running experiments quickly enough for sufficient repetitions also influenced the measurements that we chose to make. In a contact electrification experiment there could be a substantial advantage in knowing not just the net charge transferred, but also the distribution of the transferred charge (including any bipolar transfer). It was decided that using an AFM as a Kelvin Force Probe was impractical first because it could interact with the charge on the materials surface and could promote discharge, but also because it would take an excessive amount of time, relative to our goal rate, to probe a substantial portion of our $10^{-2} \times 10^{-2}$ m crystals. To overcome this we instead measured the net normal force on one crystal, and developed the techniques discussed in the experimental design and result section to infer the actual charge distribution. On the other hand our speed considerations did not compromise the contacting parameters of our experiment, in which actuators were run near their maximum speed and the time in contact, as our control experiments indicated this did not affect charging nor encourage additional discharges.

The choices made to optimize speed also had indirect effects in other design aspects of the experiment. The decision to run the experiment at a maximum of 10^{-3} Torr led to the conclusion that cleaving crystals *in-situ* was impractical, as it would not be worth the time and costs of developing an apparatus capable of this as the fresh crystal surface would immediately be exposed to an environment at high enough pressure there would be immediate contamination of this surface. Additionally, the decision to align the crystals by eye influenced the decision to include a 10^{-3} m rub in our standard procedure, as the charge transfer from a simple tap was an the lower limit of being able to detect significant differences in charging between the various material pairs.

Further practical considerations limited investigating additional parameters that would have otherwise been investigated. The effect of temperature, both differences between the crystals and absolute, on charge transfer is of interest. However, the vacuum chamber we were using was not conducive to cryogenic cooling of the crystals and heating the crystals ruled out due to difficulty in heating the crystals without risking melting the epoxy holding the crystals to their mount or damaging components in the chamber not rated to high temperatures, the difficulty in accurately measuring the temperature of the crystal surface without interfering with the experiment (which is required to monitor additional heading due to rubbing), and due to a perceived risk of having any wiring near the crystal influencing the charge transfer. It could also be enlightening to monitor material transfer between the crystals- especially in the case, unfortunately it was not possible to take *in-situ* measurements using a method such as XPS or Raman Spectroscopy or similar, and removing and transporting the crystals for analysis was not practical for the number of repetitions we required. Further it did not appear possible to measure material transfer between samples of the same material, which was a large focus of our investigation.

Material selection was again focused on repeatability and reduction of uncontrolled variables. All materials used in the experiments reported here consisted of single-crystals, both because this should reduce sample to sample variation and because it reduces variations from one point on a sample surface to another and such variations could increase fluctuations in charge transfer depending on exactly where two materials are contacting each other and could provide a mechanism for charge transfer between samples of the same material where the transfer is actually only due to differences in chemical composition or crystal orientation at individual points where contact between the samples occur. Within the category of single-crystals materials were chosen that were thought to provide stability to the experiment from one run to the next or to help isolate possible charging mechanism. The fluorides were chosen for their resistance to water, both reducing the chance that water in the contacting region could affect charging and reducing wear due to interactions with water over the course of the many repetitions. Al_2O_3, YSZ, and SiO_2 were selected as they are hard materials, and we hoped this might help put constraints on the amount charge transfer due to material transfer. All materials were received from the same manufacturer for consistency, out of their remaining available single-crystals TiO_2 was added to our set as it was still relatively inert and hard while offering a unique crystal structure.

6.3 Our Experimental Design

We describe our experiment here, which was designed taking into account the considerations above. We start with an overview such that the reader can become aquatinted with the general goal and layout of the experiment, and then describe in detail immediately after. The details of the materials used in the experiment are reported in the following section.

The goal of the experiment was to investigate contact charging between single-crystal insulators, with specific emphasis on charge exchange between like materials and the variability of that charging. To do this we designed an experiment where various such crystals could be mounted in a vacuum chamber with an operating pressure of less than 10^{-3} Torr (just over one millionth of ambient atmospheric pressure), could be repeatedly contacted with and rubbed against each other with the ability to continuously measure normal force between the crystals before, during, and after contact, and the ability to measure the charge on one of the two crystals between contacts. The system was fully automated starting at vacuum pump down, so that large numbers of contacts could be made without supervision. The specific procedure could be varied from one experiment to the next, but generally consisted of aligning flat, square crystals to achieve as flat a contact as possible, then cleaning the crystals with IPA, then closing the chamber to atmosphere to begin pump down after which the automated contacts would begin. The standard parameters were 1.5 N contacts with a 1 mm rub, for 25 contacts. Finally, at the end of each experiment the chamber was vented with gas generated from liquid nitrogen, at which point the chamber could be opened so that the procedure could begin again for the next experiment.

6.4 Equipment

The detailed set up is similar to that reported by A.L. Collins [6], but with modifications to various components. A diagram of the experimental set up is presented in Figure 6.1. The experiment is conducted in a vacuum chamber with internal dimensions measuring 15.75 inches in diameter and 7.5 inches high. The chamber is pumped down by an Alcatel ATP 80 turbomolecular pump controlled by an Alcatel ACT 200T controller, manually operated, and backed by an Edwards XDS 10 roughing pump.

Pressure is monitored by a Stanford Research Systems IGC 100 Ion Gauge Controller. With resolution of 10^{-4} Torr, with the minimum pressure detectable 10^{-4} Torr. The rub is automated by a Velmex XSlide XN10 combined stage and actuator with a 10^{-1} m linear movement range. It has an accuracy of $7.6 \cdot 10^{-5}$ m over its entire range. The contact between crystals is automated by a Thorlabs Z825BV connected to a Thorlabs stage with $2.5 \cdot 10^{-2}$ m range.

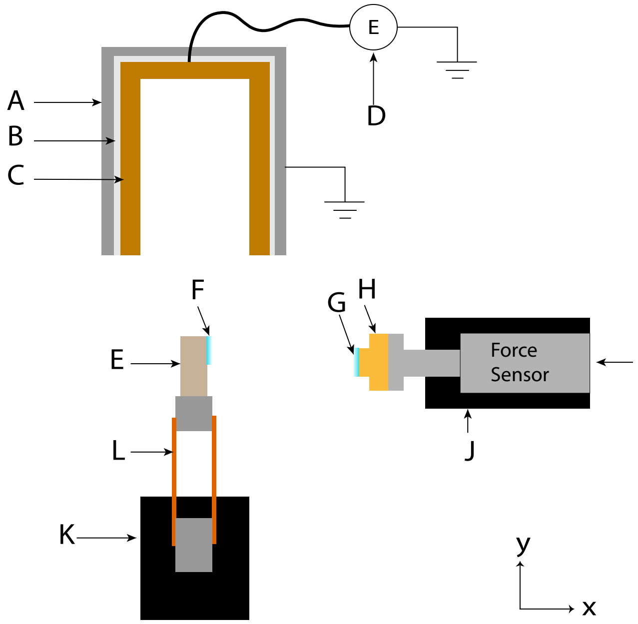

Figure 6.1: Top view of the experimental set up, this illustrative diagram is not to scale. The components of the experiment are: (A) Faraday cage to protect Faraday pail from external interference (B) epoxy between the Faraday cage and Faraday pail (C) Faraday pail, an image charge is induced proportional to the charge on the crystal inserted. A calibration is performed to get the proportionality factor (D) Electrometer through which the image charge must travel. The current is integrated to determine the image charge induced in the Faraday pail and output to the computer (E) alumina-silicate ceramic mount (F) crystal whose charge is measured, attached to the Velmex stage. We will refer to this as crystal 1 (G) crystal whose normal force is measured, attached to the Thorlabs stage. We will refer to this as crystal 2 (H) Formlabs 3D printed high temperature resin mount, attached to the force measurement apparatus (I) force measurement apparatus, a rod connecting the crystal mount to a load cell whose data is output to the computer (J) Thorlabs stage controlled by a Thorlabs controller, responsible for the contacting motion between the crystals (K) Velmex stage and actuator combination, responsible for moving crystal 1 into the Faraday pail and for rubbing motion between the crystals when applicable (L) parallel leaf spring arrangement by A.L. Collins [6], designed to resist rotating motion of crystal 1 to better maintain alignment throughout the contacting process.

The crystals are epoxied onto mounts consisting of two different materials. Crystal 1 whose charge will be measured is attached to the Velmex stage, responsible for rubbing and movement into the Faraday pail, and is mounted on fired alumina-silicate ceramic. Crystal 2 is attached to the Thorlabs stage, responsible for the tapping motion, and is mounted on a 3D printed piece made from Formlabs high temperature photopolymer resin. The mount for crystal two is coupled to a load cell in order to measure normal of on the crystal via a metallic rod. The mount is attached to the rod via three springs, which allow for a small amount of motion about three pivot points, which enables alignment of the crystals. The three pivot points consist of two thumbscrews and a ball bearing, the thumbscrews can be turned on order to change the height of their corresponding pivot points, rotating crystal 2 relative to crystal 1. It should be noted the pivot points are arranged for increased stability during contact to avoid accidental rotation, however this comes at the cost of non-perpendicular axis of rotation between the ball bearing and the thumbscrews adding difficulty to alignment. As we use rigid crystals with smoothness on the scale of 10s of Angstroms (described in the Materials section) it is not practical to optically align the two crystals at a level where there would be an appreciable contact area when they are brought together, which in turn prevents any sort of substantial charge transfer. To overcome this difficulty we add intentional compliance to the system, such that the force during contact is enough to push the crystals into alignment if un-contacted alignment is accurate enough. This compliance is introduced by capping the thumbscrews with 10^{-3} m Viton rubber, allowing for compression at those pivot points which in turn allows crystal 2 to rotate into better alignment.

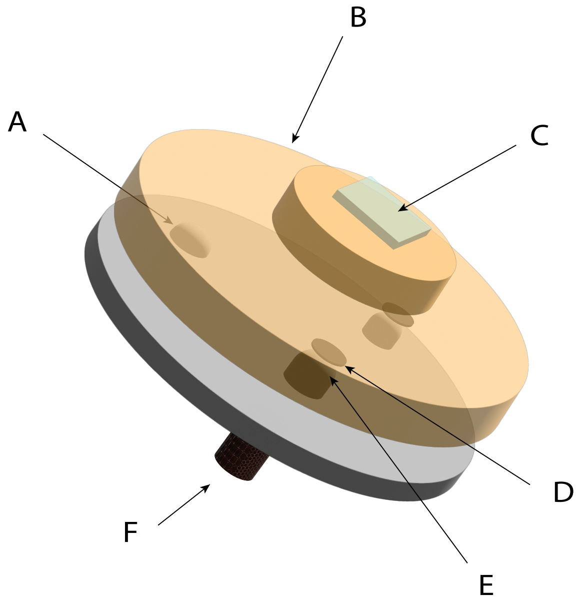

Figure 6.2: Enlarged schematic of the crystal 2 mount and alignment mechanism. (A) ball bearing which acts as one of three pivot points to align the crystal (B) the Formlabs 3D printed high temperature resin mount (C) crystal 2, attached to the mount by Stycast epoxy as described in the text (D) Viton rubber caps, placed between the thumbscrews and the mount to add compliance and increase alignment buffer (E) thumbscrews, two of them form a triangle with the ball bearing, adjusting thumbscrews allows for alignment adjustment. It should be noted the two alignment axis are not perpendicular adding difficulty to the alignment procedure but stability to the crystal when under contacting force (F) back of the thumbscrews

The total net charge on crystal 1 is measured using a Faraday pail consisting of a copper cylinder closed at one end, with a $3.8 \cdot 10^{-2}$ m diameter and a length of $5.1 \cdot 10^{-2}$ m. The Faraday pail is mounted inside a coaxial aluminum Faraday cage with a $5.1 \cdot 10^{-2}$ m diameter and $6.4 \cdot 10^{-2}$ m length. The Faraday pail is connected to a Keithley 6514 electrometer, which integrates current to the Faraday pail, outputting the induced image charge to the experimental computer. The integrated charge drift is less than 10^{-11} C/hour.

The force sensor arrangement remains unchanged from the description A.L. Collins provides "An Omegadyne LCFL-10 tension/compression load cell with 10 lbf capacity is mounted axially to a 5/8 in. diameter, 2.75 in. long stainless steel rod, upon which the ABS anvil is mounted... The steel rod is held axially with a linear ball bearing to reduce any non-normal forces reaching the load cell. The output of the load cell is amplified with a Tokyo Sokki Kenkyujo Co. Ltd. DC-96A dynamic strainmeter, where a 30 Hz low-pass filter is applied to the voltage output." [6]. This force sensor's utility is two-fold, first it allows us to measure the normal force between the crystals when they are in contact, allowing for compare and standardize contacts from one experiment to the next, and second it allows us to probe the charge distribution on the crystals based on the force-distance curve upon approach or pull-off. The charge probing method is described in the procedure and result sections.

A second vacuum chamber is used to cure the epoxy when the crystals are first attached to their mounts. Its vacuum is maintained by an Edwards nXDS-6i scroll pump.

6.5 Procedure

Our experimental procedure is described in detail here, using the equipment described above, and designed with the considerations outlined above.

In all of the falling, any time the experimental chamber is not under vacuum there is nitrogen, from the gas use valve of a liquid nitrogen dewar, flowing through the chamber. The flow rate is not high enough to stop atmosphere from entering the chamber, but dramatically reduces the pump down times for when the chamber is open for limited time. This leads us to believe it is helping to reduce water absorption onto the surface of the vacuum chamber wall, as well as surfaces of the objects inside, and we have no reason to believe this would not include the interacting surfaces of the crystals that we are investigating.

When putting in new crystals the Loctite Stycast 1266 epoxy which will be used to mount the crystals is mixed, degassed as recommended, then a small amount (less than a drop to insure the epoxy cannot reach the front side of the crystal during curing) is placed on each of the crystal mount surfaces. The MTI Corporation crystals are removed from their storage desiccator and removed from the sealed plastic container they are shipped in by non-marring tweezers and are immediately placed on the epoxy in the ambient laboratory environment. The crystal whose charge will be measured is mounted on alumina-silicate ceramic and he other crystal is mounted on the 3D printed piece. They are then gently pressed into the mount with the tweezers and the mount with crystal are moved into a curing vacuum chamber where the epoxy is allowed to cure in vacuum at room temperature for 24 hours. The mounts with their crystals are then removed from the curing chamber and transferred to the experimental chamber where the mounts are attached to their respective stages. The crystals are then manually wiped with an IPA (Sigma-Aldrich $< 99.9\%$) folded and soaked Thorlabs MC-5 lens tissue, held with conductive forceps, to clean the surface. At this point the experiment is ready be run per the prescribed procedure for that individual experiment.

With the crystals mounted in the chamber, if an experiment is to undergo alignment the crystals are brought close to each other. In our standard procedure for the self-charging experiments the crystals are actually brought into contact and then the alignment thumbscrews are adjusted until no light can be seen between the crystals by eye (previously we used two cameras to view the crystals at right angles, but there no evidence this was improving the alignment, while it did significantly increase the time the experimental chamber was exposed to ambient atmosphere). Additionally, we looked for a sign of a slight adhesion force upon separating the crystals which was thought to indicate better alignment. Although not part of our standard procedure, it was also possible to do this alignment by bring the crystals about 10^{-4} m from each other and adjusting the alignment thumbscrews until the crystals appeared parallel from both angles perpendicular to the axis of rotation created by the pivot point and the thumbscrews. This alternate procedure was valuable for experiments where two fresh crystals of dissimilar materials were going to be contacting each other for the first time and we wanted to avoid any interaction between the materials prior to the controlled experimental contacts in vacuum.

After alignment, when applicable, the crystals would again be cleaned with IPA soaked

Thorlabs tissue for the standard procedure. This is a modification of the procedure by A.L. Collins from our group [6], and its effectiveness has been discussed by W.R. Harper [79]. Our experiment is conducted in a standard laboratory at UCLA, without clean room procedures it is likely that microscopic contaminates remain or attach to the surface before the chamber can be sealed and pumped down to vacuum. It was also possible to apply other liquids to the crystal surfaces using this procedure if desired. The apparatus is designed to cycle between atmosphere and vacuum as rapidly as possible in order to maximize the rate that one run can be completed and the next begun. To do this both the turbomolecular and roughing pumps are always running. At the beginning of pump down the chamber is sealed and the outlet of the turbomolecular pump is sealed from the inlet of the roughing pump. Then the inlet of the roughing pump is opened to the experimental chamber and nitrogen is allowed to continue to flow until the pressure reaches roughly 300 Torr in order to help flush out condensible vapors. At this point the nitrogen flow valve is sealed and the chamber would be pumped down to $2 \cdot 10^{-1}$ Torr by the Edwards roughing pump. At this point the inlet of the roughing pump is sealed from the chamber and is opened to the outlet of the turbomolecular pump, and the turbomolecular pump inlet is opened to the chamber. This configuration is maintained for the rest of pump down and during the experiment. From the point the turbomolecular pump has taken over pump down the computer completely runs the experiment as described below, until the run is finished. When the investigator is ready to set up the next experiment the inlet of the turbomolecular pump is sealed from the experimental chamber and is kept running, while the chamber is vented with nitrogen gas which continues to flow until the next pump down procedure begins.

Once the computer takes control of the experiment it first monitors the pressure via the SI ion gauge controller, and records a pressure versus time curve, sampling once every five seconds, which can act as a proxy for determining the state of water absorption on the surface of the materials inside the chamber. Once the operating pressure set by the investigator is reached (set to 10^{-3} Torr for our standard procedure) the contact electrification experiment begins. For the duration of the experiment the chamber pressure is measured prior to each contacting procedure, allowing for later analysis to account for any instability in the ambient environment during the experiment. Before the crystals contact each other the crystal mounted on the Velmex stage is inserted into the Faraday pail in order to measure the residual charge that might have been deposited during cleaning or incidentally transferred from the atmosphere while the chamber is open. This residual charge is subtracted from the rest of the measurements to indicate only the transferred charge. Of course if the residual charge is large it must be considered in any force measurements or discharge calculations, there would be an added difficulty in such cases as the residual charge is not guaranteed, or even likely, to be equal and opposite on the crystal that is not inserted into the Faraday pail. Fortunately, in the experiments reported the residual charge is never found to be large enough to affect either the force or discharge calculations.

After the residual is measured the first contact takes place. The Thorlabs stage is capable of moving 25 mm as the actuators maximum speed of 2.2 mm/s. The Velmex stage is the one responsible for the rub, its range is longer than the 10^{-1} m length of the crystal any rub distance desired is achievable. Further, the program running the experiment has been designed to set the initial position, point of contact, point of separation, and final position of both stages. This allows the investigator to run everything from a simple tap, to a bi-directional asymmetric rub with a different final separation distance to control discharges. For our standard procedure the crystals are contacted at a distance that gives a force near 1.5 N (the force can vary from contact to contact and run to run due to intentional compliance in the system discussed in the equipment section) with an approach and contacting speed of 2 mm/s then rubbed 10^{-3} m in one direction, then rubbed 10^{-3} m in the opposite direction so the crystals are back in their original contact position, then finally the crystal on the Thorlabs stage is returned to its initial position. During this entire process the normal force on the Thorlabs crystal is being sampled (at 10^3 Hz in the standard procedure. After the contact is complete the crystal on the Velmex stage is again inserted into the Faraday pail in order to measure the charge transfer, then both crystals are returned to their initial positions. This contacting portion of the experiment is completely customizable and can be modified in real time, so for example the investigator is able to do alternating 1 *mm* rub contacts and just tapping contacts to better understand the contribution of the rub.

In our standard procedure we complete this contacting procedure 25 times in a row, before breaking vacuum to set up the next run. For each pair of crystals the standard procedure involved ten runs, the first run the fresh crystals go through their initial alignment as they have just been mounted in the chamber, then for the following runs we follow the pattern of realigning on the first run of the sub-series, then complete two runs without any realignment, just cleaning the crystals with the IPA, then start the next sub series. We complete the sub-series three times so in total there are alignments/realignments on the first, second, fifth, and eight runs. The reason for realignment on the second run instead of completing a sub-series is that due to the intentional compliance in the contact (as mentioned in the equipment section) there was often poor charging during the first run as the system settled into position due to the repeated contacts and the effects of being in vacuum, or this settling would lower the charging in the second run. This was observed not only for fresh crystals, but any time the crystal mounts were removed and put back into the chamber, so the reduced charging is not unique to fresh crystals and thus unlikely to be the effect of some sort of crystal fatigue or material transfer inhibiting the charging.

6.6 Force Probe and Simulation

We designed our experiment in such a way that the normal force on one of the crystals would be measured at a rate of 1 kHz (the sampling rate could be increased if desired) as the crystal approached the other, during the contact and rub (when applicable), and during recession. This not only serves the purpose of allowing us to monitor the force of contact, but also allows us to monitor the force of attraction on approach and on pull-off, which we argue not only allows us to detect the presence of charge transfer when an attractive force is observed, but actually allows us to probe the details of the charge distribution on the crystals based on how this force changes as a function of distance. The advantage and details of this probing mechanism is discussed in the results and discussion sections.

To understand the details of the charge distribution on the crystals in an experiment we ran a COMSOL finite element simulation to determine the normal force and potential between the two crystals based on various possible charge distributions on the material surfaces. The simulation was run for various distances between the crystals to get a force versus distance plot that could be compared to our actual experimental results. The boundary condition for the simulation was a grounded conducting cylinder with $2 \cdot 10^{-2}\ m$ radius and $6 \cdot 10^{-2}\ m$ length. The crystals were modeled as dielectric squares with dimensions $1 \cdot 10^{-2}$ $m \times 1 \cdot 10^{-2}\ m \times 5 \cdot 10^{-4}\ m$, matching the physical crystals used in our experiment.

The time it takes to run a COMSOL simulation prevents us from running every parameter choice we would like, so the parameters we used and described here are the subset we believed would be most useful. Methods to extrapolate our COMSOL results to better match the actual parameters of our experiment are discussed below. Both the normal force between the crystals and the potential between the center of each crystal was calculated in a COMSOL finite element simulation for the each combination of the following parameters. Distance between the crystal faces was set from 10^{-6} to $5 \cdot 10^{-5}\ m$ in increments of $5 \cdot 10^{-6}\ m$, then from 10^{-4} to $10^{-3}\ m$ in steps of $5 \cdot 10^{-5}\ m$. The crystals were assigned relative permittivities, ϵ_r, of 1 (to simulate a patch of charge in vacuum, rather than attached to the surface of one of our crystals), 6.81, and 10.4. The total charge on each crystal face (with opposite polarities) was set to $5 \cdot 10^{-10}$, $1 \cdot 10^{-9}$, $1.5 \cdot 10^{-9}$, $2 \cdot 10^{-9}$, $5 \cdot 10^{-9}$, and $1 \cdot 10^{-8}\ C$. The patches of charge were set to have matching radii of 0.001, 0.002, 0.003, 0.004 and 0.005 m, and the charge density of the patch is constant. Note that the simulation does take into account any induced surface charge on *all* faces of the crystal, not just the closest face.

COMSOL takes time to run each step in a force or potential versus distance plot, that is the simulation must recalculate the force if any parameter is changed, including the distance between the crystals. This is critical as this is where our experimental data is most abundant, a single contact will have fixed charge, fixed charge distribution, and fixed permittivity for each crystals, but will have 500 hundred data points in the closest 1 mm to contact alone, and that number can easily be increased if desired. For this reason it is important to find ways to decrease the number of calculations COMSOL must compute, so it was effort was made to find which parameters we could analytically extrapolate from a single COMSOL configuration to others. If successful this would enable us to run a single parameter set, only changing distance between the crystals in each calculation, and then use our analytical method to predict what the force should be for a different configuration of parameters. This is important as it is not practical to use COMSOL to compute ever possible configuration to match our experimental results. For example one might have run COMSOL for two contacting crystals with the same permittivity as $\mathrm{CaF_2}$, with charge in 1 mm radius patches, with a total charge of between 1 and 10 nC in steps of 0.5 nC, but if in the experiment the actual charge is 3.14 nC then the ability to make a precise comparison to learn something about the charge distribution is lost. We found that for the simulation force results, F_i for a given total charge, q_i, a new total charge, q_f, results in a new force given by $F_f = \left(\frac{q_f}{q_i}\right)^2 F_i$. An example is shown in Figure 6.3 showing an original COMSOL force plot and four predicted force curves with new charges, and plotted with COMSOL simulations of the new charges to verify the accuracy and consistency of this method. We found the predictions of this method to be consistently in agreement with COMSOL results for the new charge, with an accuracy described by less than $7 \cdot 10^{-11}$ % error between the two force predictions. We believe the consistency at this level justifies extrapolation of COMSOL results to arbitrary total charge in our experimental range.

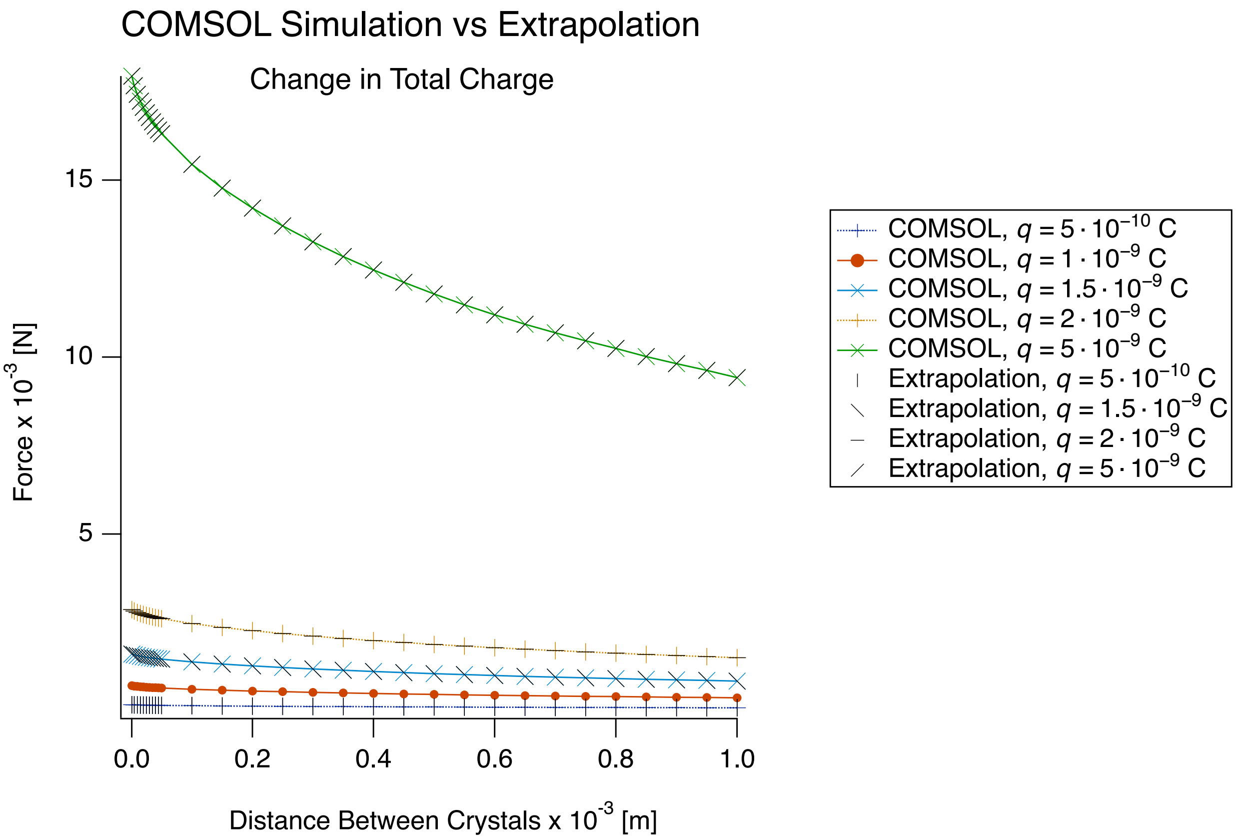

Figure 6.3: COMSOL simulation for equal and opposite patches of charge with radii $5 \cdot 10^{-3}$ m on crystals with relative permittivity 10.4, with varying total charge. Presented are COMSOL calculations for five total charges, and our extrapolations for the same total charges based only on the COMSOL results for the $1 \cdot 10^{-9}$ C simulation. Our extrapolations are in agreement with the COMSOL simulation described by less than $7 \cdot 10^{-11}$ % error between the two force predictions, suggesting we can use this method to expand our COMSOL results to arbitrary charge with all other parameters equal. The extrapolations are plotted as half of the 'x' or '+' symbol of the same point marked by COMSOL result to illustrate how precise the overlap is.

In Figure 6.4 the COMSOL results are plotted for various permittivities. At this point we have not developed a method to extrapolate the force between crystals with one set of permittivities from a COMSOL simulation using crystals of another set of permittivities.

Qualitatively, the trend is increasing permittivity reduces the force between crystals at larger distances, and the force appears to converge when the crystals are very close together. This is reasonable as while the total charge on the crystal is independent of the relative permittivity for a given patch of charge on the surface, the induced bound charge from that patch on the near surface is greater for larger permittivity. The net charge on the near surface is given by $q_t = q_b + q_i = \left(1 - \frac{\epsilon_r - 1}{\epsilon_r + 1}\right)$, with q_b the induced bound charge and q_i the fixed patch of charge. The charge density follows the same relative distribution as the fixed patch, which for us is constant. The reduced charge on the front surface is exactly compensated by increased charge on the far surface, but the closest surface will have a larger effect on force and thus we expect to see reduced force at a distance. The convergence of force for the different dielectric pairs near contact is also expected. As the crystals come into contact the equal and opposite patch from the opposite crystal will induce a bound charge exactly equal and opposite to the original bound charge induced from the charge on that crystals surface. Since the bound charge exactly cancels out, the result should be a force that is independent of the bound charge and thus independent of the relative permittivities of the crystals. This dependence on distance complicates the extrapolation from one pair of permittivities to another.

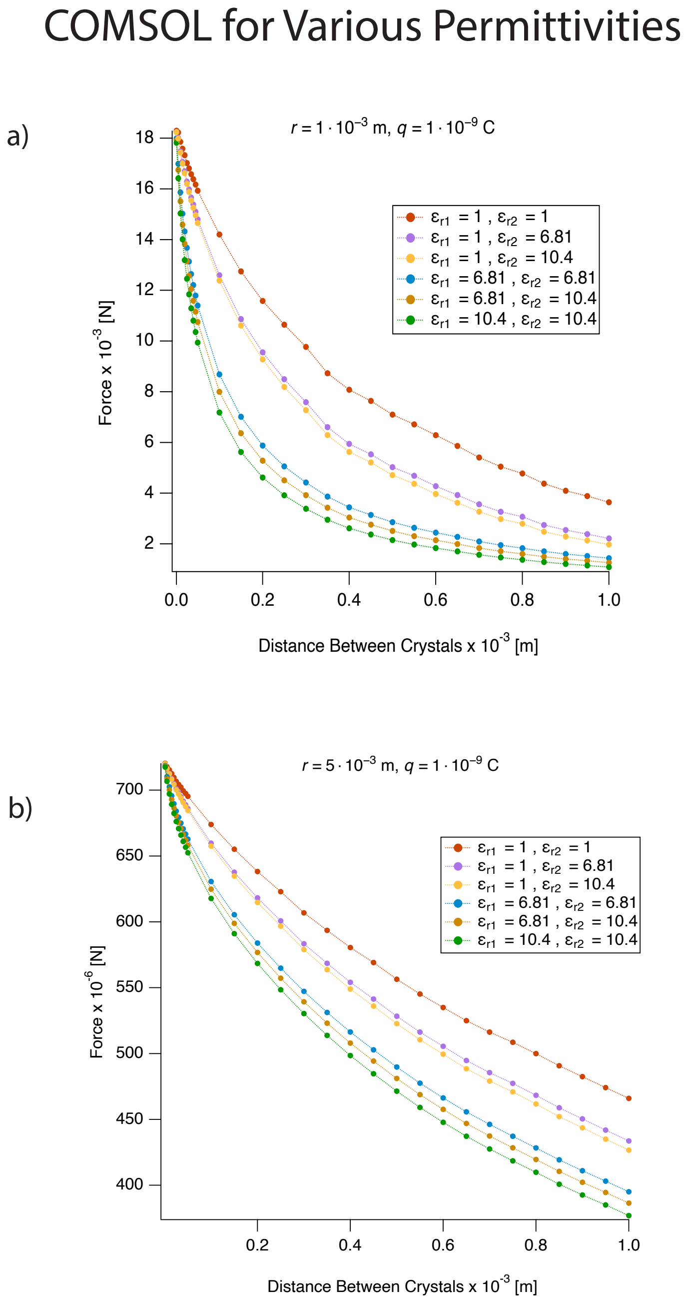

Figure 6.4: COMSOL results for two crystals with equal and opposite patches of charge with $1 \cdot 10^{-9}$ C total charge magnitude with (a) $1 \cdot 10^{-3}$ m radii and (b) $1 \cdot 10^{-3}$ m. The curves are the combinations of $\epsilon_r = 1$, 6.81, and 10.4, that were simulated, with $\epsilon_r = 1$ corresponding to a patch charge in vacuum.

We also looked into our ability to extrapolate force due to charge patch sizes different than the ones used in the COMSOL simulations. We have already shown that we can extrapolate the force due to new total charges, which effectively allows us to choose a charge density, but as in the experiment the total charge is locked, a reliable comparison between the simulation and experimental results require the ability to select arbitrary patch size. We attempted our extrapolation by looking for a relationship between parameters of two different configurations with different patch sizes that would give the same force. If this relationship could be found, then our ability to extrapolate to arbitrary charge would allow us to plot a new force curve for any patch size at our desired total charge, only noting that our distances between the crystals might be shifted, but without a loss in the number of data points. Since the force on a point charge, q, is given by $F = qE$ and at close distance we expect the electric field, E, to be proportional to the charge density, which is given by $\sigma = \frac{q}{r^2}$, with r the patch radius, then we expect $F \propto \frac{q^2}{r^2}$. Thus, to keep the force the same between two parameter points we will multiply both the original parameters for charge and patch radius by the same constant. At the same time $\frac{r}{d}$ appears to be a relevant dimensionless quantity as it relates to the relevant angles and the force should increase with r^2 due to increased total charge (from our decision to keep $\frac{q}{r}$ constant), but force should decrease with d^2 as the distance between each element of surface charge increases. This doesn't guarantee the force will be the same between two parameter points where r, d, and q are all multiplied by the same constant, but provides motivation to check if this is the case. Figure 6.5 shows the results of this extrapolation. As can be seen in the figure the prediction does offer a rough match to the results from COMSOL for the new parameters, but the values are significantly off with relative error as high as 3%. Still the accuracy here is better than the precision of our experimental force measurements, so this method can be used to see if there is an approximate match between our experimental results and this extrapolation to give an estimate of the charge patch size on the crystals.

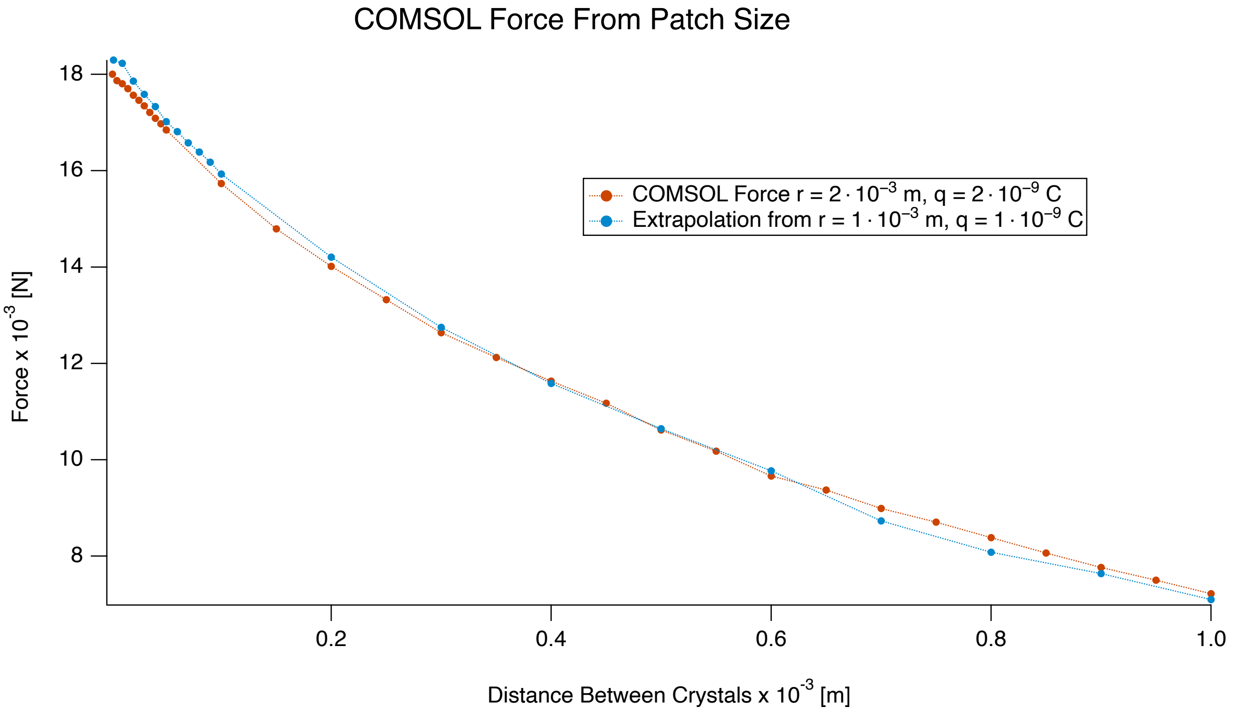

Figure 6.5: COMSOL results for two crystals with equal and opposite patches of charge with $2 \cdot 10^{-9}$ C total charge magnitude and $2 \cdot 10^{-3}$ m radii plotted against our extrapolation from the COMSOL results for a patches of charge with $1 \cdot 10^{-9}$ C total charge magnitude and $1 \cdot 10^{-3}$ m radii. The extrapolation has been plotted at twice the crystal separation distances from the original simulation, ensuring that r, d, and q have all been multiplied by the same factor of two. The relative permittivity of the crystals is set to $\epsilon_r = 1$ to eliminate the crystal thickness as a possible length scale.

These configurations and parameter ranges are obviously not all-encompassing, but rather are used as a starting point to identify features of the charge distribution arising from contact electrification. Other parameters and configurations that were not included in the simulation are discussed in the results and discussion sections.

6.7 Materials

In our experiments we use macroscopic single-crystals as listed in Table 6.1 with various material properties. The crystals are from MTI Corporation and are stored in a desiccator connected to the building vacuum line until ready to be mounted and used in our experiments. The crystals had $10^{-2}\ m \times 10^{-2}\ m$ square faces, with a depth of $5 \cdot 10^{-4}\ m$.

Table 6.1: List of Material Properties Used in Our Self-Charging Experiment. YSZ is yttria-stablalized zirconia, ZrO_2 stabilized with 8% by mole Y_2O_3. Data is provided by the crystal suppliers, MTI Corporation, unless otherwise specified. Surface roughness is measured by arithmetic mean for all samples but YSZ which is measured by root-mean-square.

Material	**Dielectric Constant** ϵ_r	**Crystal Structure**	**Crystal Orientation**	**Surface Roughness** Å (Ra)
Al_2O_3	11.58	Hexagonal	(0001) $\pm 0.5^o$	< 5
SiO_2	4.64 [80]	Hexagonal	(0001)	< 5
CaF_2	6.8 [81]	Cubic	(100) $\pm 1.5^o$	< 25
TiO_2	114 [82]	Tetragonal	(100)	< 5
YSZ	27	Face Centered Cubic	(100) $\pm 0.5^o$	< 5 Rms
BaF_2	7.4 [81]	Cubic	(100)	< 20

CHAPTER 7

Discussion and Future Experiments

We now present the detailed results of our experiments. These findings can be broken up into two main pieces, our observations of charge transfer between two identical single-crystals, and the results concerning a way to probe the transferred charge distribution using force data. Both have been covered briefly in the introduction, we will repeat the key points here while more thoroughly commenting on our results and their implications. Finally, we will propose future experiments that we believe will provide the basis for rapidly developing a comprehensive theory of contact electrification.

7.1 Self-Charging Results

The first key result was our observation of self-charging between identical, planar single-crystals, which builds upon previously reported experiments between asymmetric samples of the same material or between polymers of the same shape. The significance of using single-crystals is we eliminate the large variability from one point on a material's surface to another that exists for polymers, create a much more repeatable surface and have a clear orientation for the bulk, have surfaces much more resistant to deformation as they will maintain their crystal structure, as well as allowing for much flatter surfaces which are smooth at level of a few atomic layers (see Table 6.1). The advantage of the plane geometry is we eliminate any intentional asymmetry that could lead to charge transfer, which puts new bounds on theories attempting to explain contact electrification.

We observe clear non-zero charge transfer for all pairs of crystals in our experiments, attaining charge transfer above the 1nC level for CaF_2, SiO_2, TiO_2, and YSZ, and with peaks of $0.3nC$ for BaF_2 and $0.08nC$ for Al_2O_3. Already having four of the six crystals charge to such high levels is extremely significant, but this is made even more so with careful inspection of the YSZ self-charging data. The YSZ pair actually did not exhibit charge transfer above $0.25nC$ until the final sub-set. This data, along with our data from other self-charging pairs and from pairs of dissimilar single-crystals suggests that the alignment at the beginning of each sub-set has a dominating effect on charge transfer. This then implies that BaF_2 and Al_2O_3 could exhibit similarly large charging if the experiment were repeated with more realignments.

One explanation for our observations of charge transfer between identical single-crystals would be that there is some asymmetry in the nature of our contact, and that asymmetry is what enables a net charge transfer in one direction or another. There are a range of mechanisms in which the asymmetrical contact could enable charge transfer, for example one crystal now gets heated more than the other or the pressure on one crystal is larger which enables causes it to transfer material to the opposite surface. Independently of the exact mechanism it is worth noting that in several sets of our experiments for same material self-charging we observe polarity flips from one run to the next, even when there is no realignment between runs. This indicates if there is some asymmetry in our contact, it is either not responsible for the charging polarity, or varies so much from one run to the next, even without any intentional realignment, that it can completely alter the polarity of net charge transfer. If the latter were the case one would expect instances of dramatic polarity reversals from one contact to the next in a given run as we have just claimed the change in alignment is so small it should be able to occur at random. This is never observed so it seems that an asymmetrical contact is not responsible for the observed self-charging. It is worth clarifying that if the charge transfer is driven by a nucleation style mechanism based on some initial charge on the material surfaces, then an asymmetry could be responsible for that initial charge, but it seems to be impossible it is responsible for the continuing charge transfer that would be the fundamental mechanism behind contact electrification.

7.2 Results from the Charge Distribution Probe

In addition to the raw charging data, our experiment was designed in such a manner to allow for continuous measurement of the force between the crystals, orthogonal to the crystal surface, both arising from the attractive force between charges of opposite polarities which exists as the crystals approach each other and during separation, and from the normal force during contact. The force during contact can be used to ensure our contacts from one experiment to the next are is similar as possible, but it is the attractive force during approach that we found most intriguing as it provided a method of probing not only the net charge on the crystals, but the actual charge distribution on the crystal surfaces. This analysis of the normal force between crystals has allowed us to infer information about the charge distribution on the crystal surface after contact electrification in a non-invasive technique that neither takes additional time nor has the possibility of altering the surface charge. Figure 7.1 shows our experimental force results for a contact between Al_2O_3 and SiO_2 compared to COMSOL finite element simulations for various parameters. In our COMSOL simulations we are able to match the dielectric strengths of the crystals as well as vary the size of the charge patch and the net charge on each crystal. Further, we were able to plot the effect of bipolar charging on the force versus distance curve. By changing these parameters and comparing to experimental results we are able to gain detailed information about the charge distribution on the surface of the crystals. The effect of varying these parameters was discussed in the methods section. Comparing Figure 7.1 to Figure 7.2 and Figure 7.3 it can be seen that the experimental data for Al_2O_3 vs SiO_2 is fairly well fit bit charging of single polarity, particularly at larger distances, where as the experimental data for CaF_2 versus CaF_2 has an obviously lower force at large distances. This suggests that while bipolar charging is likely needed to better fit the Al_2O_3 vs SiO_2 data for small separation distances, the amount of bipolar charging is likely much less in the case of Al_2O_3 vs SiO_2 compared to the self-charging of CaF_2 vs CaF_2. Figure 7.3 emphasizes how well the bipolar charging data can fit self-charging data, but here the COMSOL data is using a smaller net charge than the net charge from the experimental data. This leads to the discrepancy at large separation distances, but is consistent with the idea that small separation distances are well modeled with bipolar charging, but the number of patches needs to be increased to accurately match the entire curve. For this reason we believe the force probe method can provide a highly accurate depiction of the surface charge distribution on the crystals, with the only limitation being the amount of COMSOL data to compare and find a match with (that is to say, limited by computer time of running the simulations) and reasonable sensitivity of the force probe. The force probe sensitivity is less critical than in other applications as the analysis does not rely on a single data point but on the shape of the entire force curve as a function of distance. As stated previously, the key to this level of detail is that we are not examining only the maximum attractive force or the force at some set distance, but instead we measure the entire curve at arbitrary sampling rate, and this allows for a description better than AFM as it can probe larger areas in less and is non-interfering while still giving highly detailed information on the charge distribution. Thus it seems this technique, with an adequate COMSOL library and the extrapolation techniques discussed in the methods section, should be able to provide near perfect description of the charge distribution, with only symmetry based ambiguity, which can be resolved by rotating or translating one crystal relative to the other on approach.

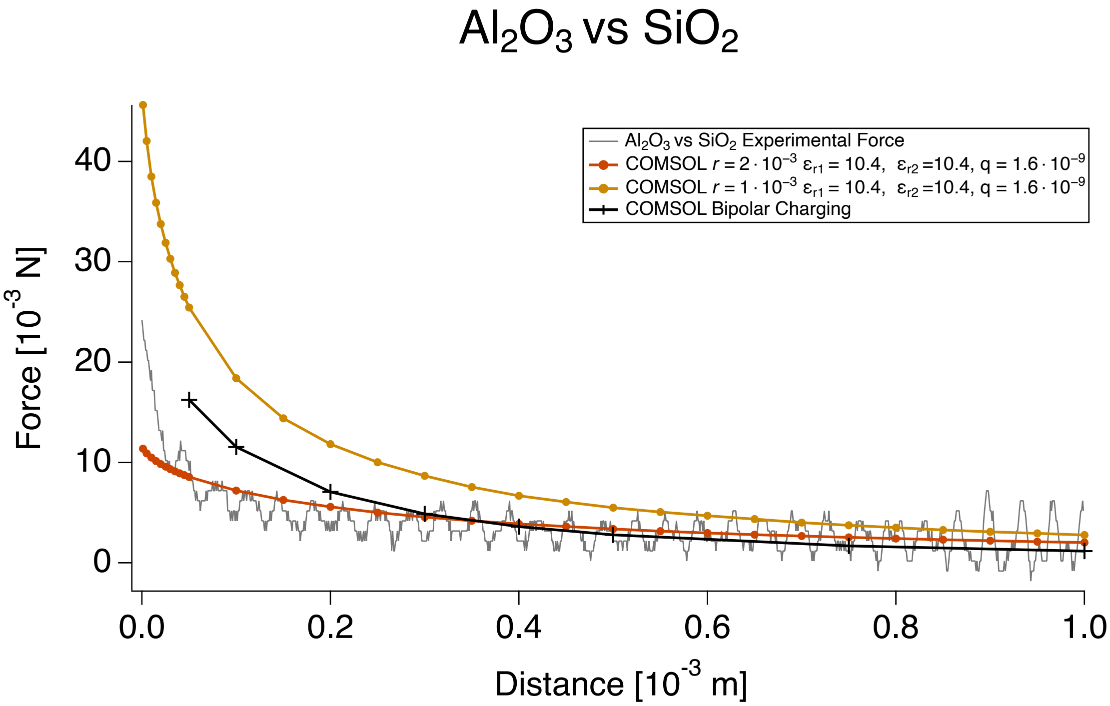

Figure 7.1: Al_2O_3 vs SiO_2 experimental results compared to COMSOL finite element simulations for multiple parameters. The red and yellow dots are COMSOL simulations that demonstrate how the charge patch size can change the force profile as a function of distance for the same total charge. The green cross shows COMSOL results for bipolar charging. Note how the bipolar charging is able to achieve a larger peak force at close distances than the larger mono-polar charging, while still having a lower magnitude of force at large distances.The bipolar charging appears to trend towards under-predicting the force magnitude at large separation distances.

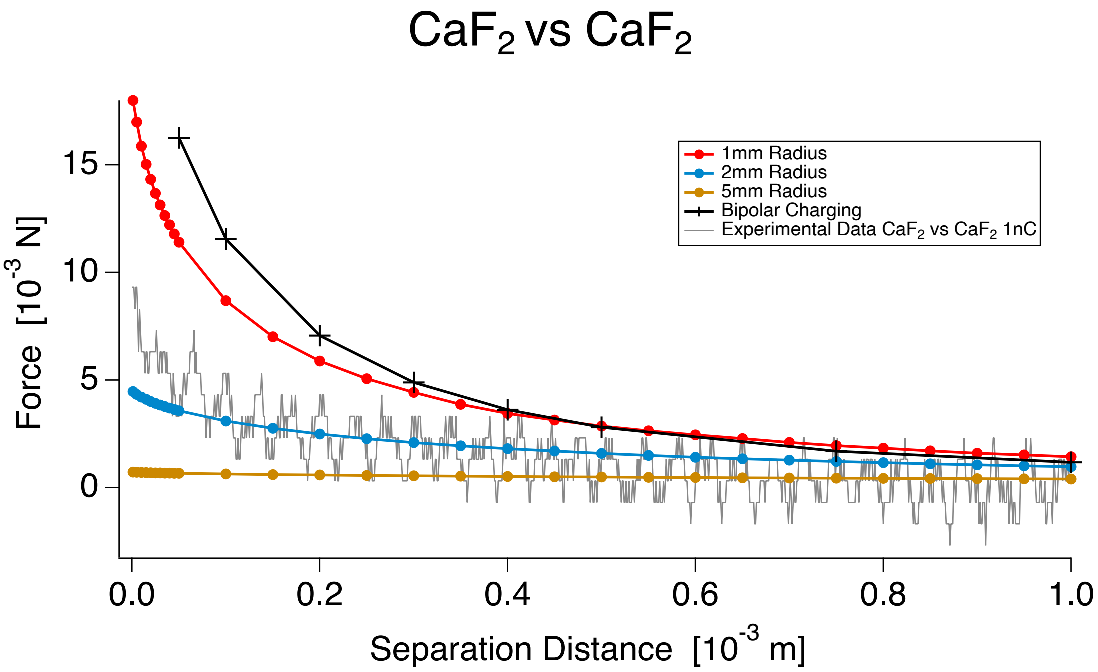

Figure 7.2: CaF_2 vs CaF_2 experimental results compared to COMSOL finite element simulations for multiple parameters. Here COMSOL results are presented for various patch sizes with a total charge of 1 nC for singe polarity charging and for bipolar charging of two patches of 1.5 nC and two oppositely charged patches of 1 nC for a net charge also of 1 nC, each with a radius of $2 \cdot 10^{-3}$ m. The $5 \cdot 10^{-3}$ m patch matches the experimental force at large separation distances more accurately, but strongly diverges at small separation distances. Smaller patch sizes can bring the fit closer to the experimental data at small separation distances but clearly predict too large of a force at large separation. The bipolar charging does not match the experimental data well, but is shown here to illustrate how it can have a larger peak force than a single patch of charge at small separation and a lower force at large separation, which is the trend required to match the experimental data.

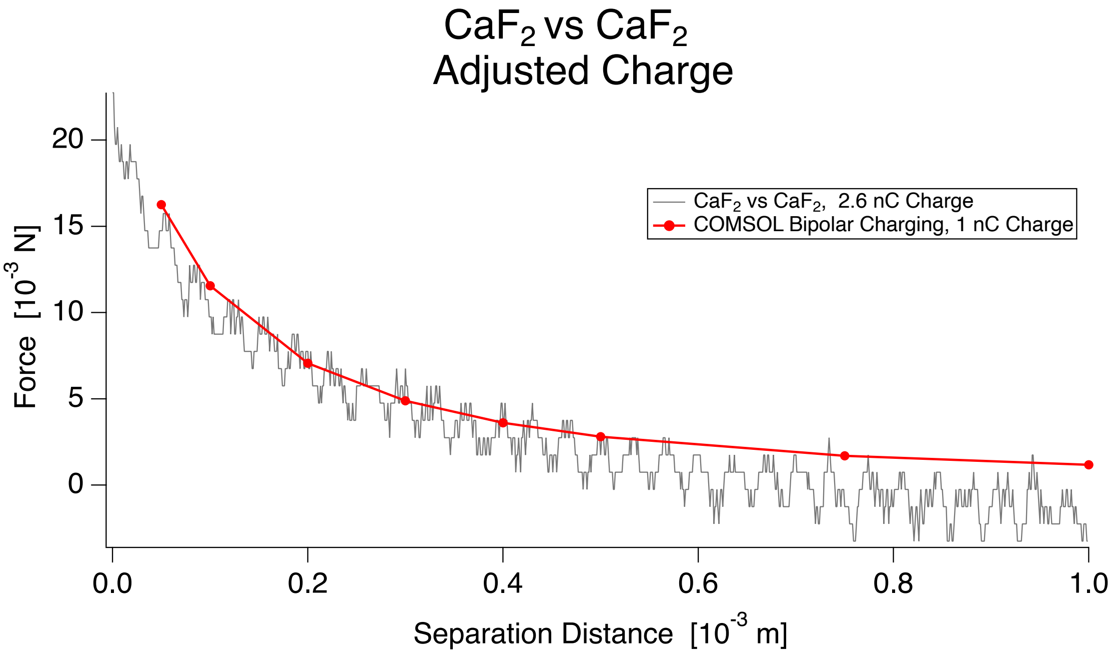

Figure 7.3: CaF$_2$ vs CaF$_2$ experimental results for 2.6 nC net charge compared to COMSOL finite element simulations for bipolar charging with 1nC net charge. The bipolar charging is four patches of 2mm radius, two with 1.5 nC of charge and two oppositely charge each with a charge magnitude of 1nC.

As the peak force is determined entirely by the net charge density, independent of polarity, it is useful to know how charge density and patch size evolve over time. Figure 7.4 shows how our calculated charge density evolves over a large number of contacts and Figure 7.5 shows the corresponding correlation between patch size and the net charge. Together the results indicate that initially charge density grows while the patch size varies within some range, but then there becomes a clear correlation with patch size and the total charge. This suggests at some density threshold the net charge starts to grow as a result of increasing patch size rather than increasing charge density. It is possible that this correlation is simply the result of a discharge threshold for the electric field which in turn is based on the charge density. However, it is interesting that the increase in charge at the beginning seems to be dominated by charge density increase when there would be no limit on the size of the patch increasing.

To emphasize the utility of our new probing technique Figure 7.6 shows the evolution of the force curve in one of our experiments. The plot shows two contacts (contact two and contact six) where the charge has increased by a factor of ~ 2.1. The maximum force appears to fall off from the $2mm$ simulation, suggesting that the patch size has increased, and is between $2mm$ and $3mm$ in radius. However, the benefit of probing technique presented in this thesis is demonstrated at larger separations where although the patch radius is still bound by the $2mm$ and $3mm$ curves, the experimental data clearly deviates from either curve, suggesting that the charge distribution is not a simple single patch. The shape and evolution of the curve between the two contacts shows consistency while still demonstrating the probes ability to monitor changes in the charge distribution. Figure 7.7 shows the same evolution for SiO_2 contacting YSZ. These two plots are illustrative examples of over 200 plots we created to analyze the evolution of charge patches for each or our crystal pairs. Both for the single point analysis and analysis using the force probe technique, these results are consistent with a charge nucleation description where initially charge is able to build up locally at seed sites, before crossing some threshold where the patches can begin to grow along the surface and additional charge transfer is due to patch growth.

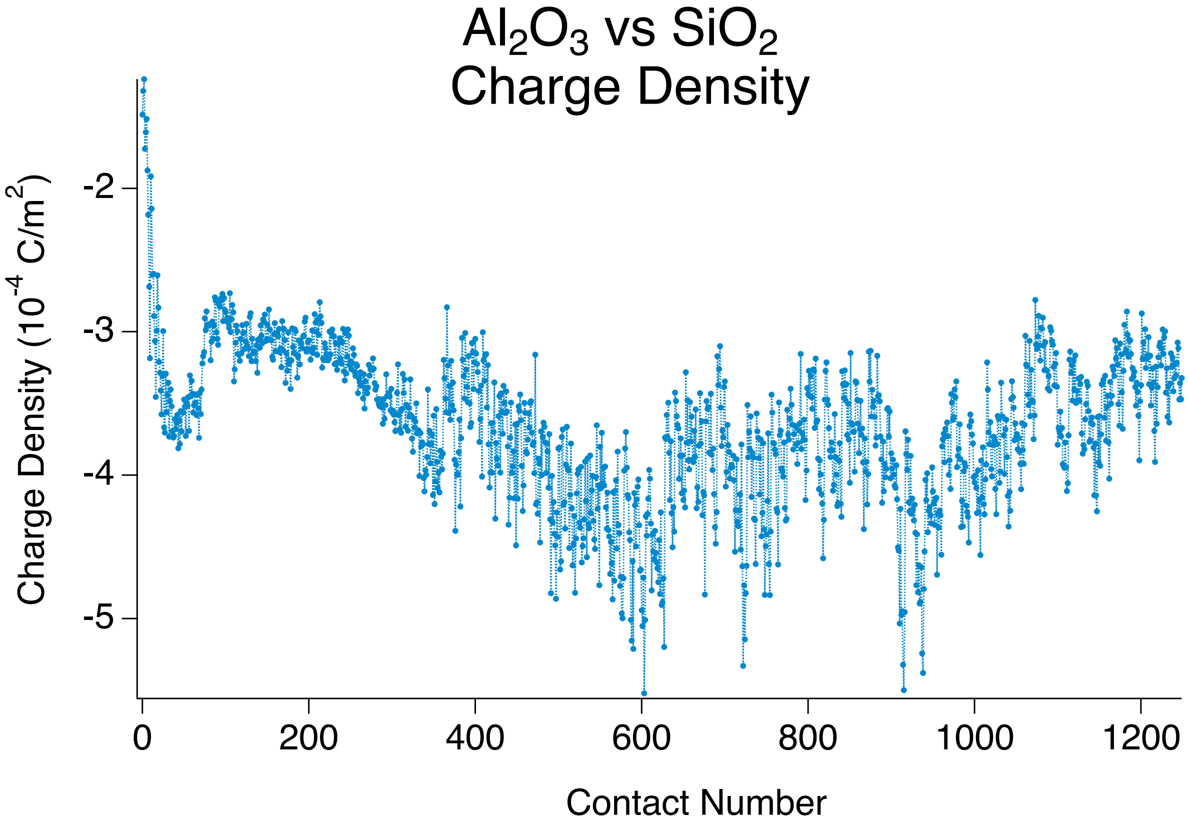

Figure 7.4: Charge density during an extended run with Al_2O_3 contacting SiO_2. The charge density is calculated using the maximum attractive force, which occurs just before the crystals make contact.

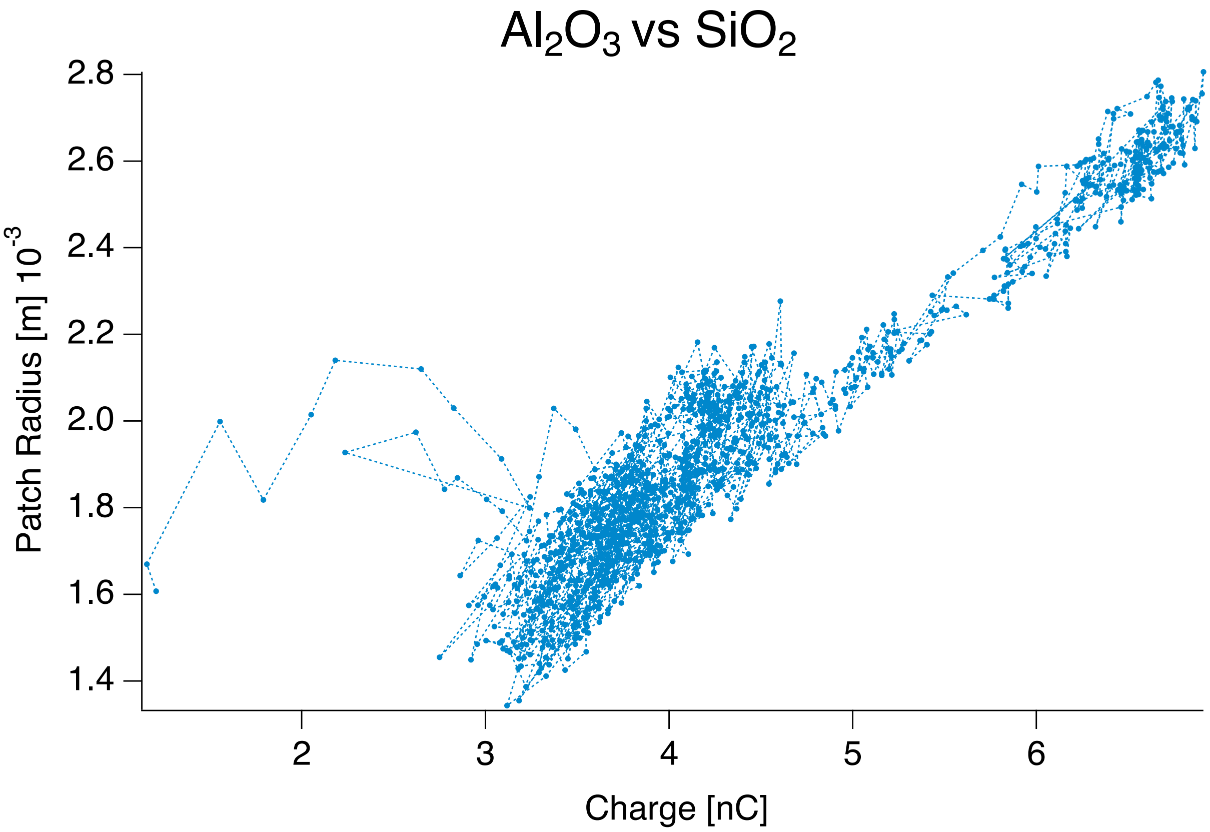

Figure 7.5: Plot of our calculated charge patch radius vs net charge measured on one of the crystals. The data comes from Al_2O_3 contacting SiO_2, and the calculation is based on the maximum attractive force between the crystals, occurring just before the crystals make contact.

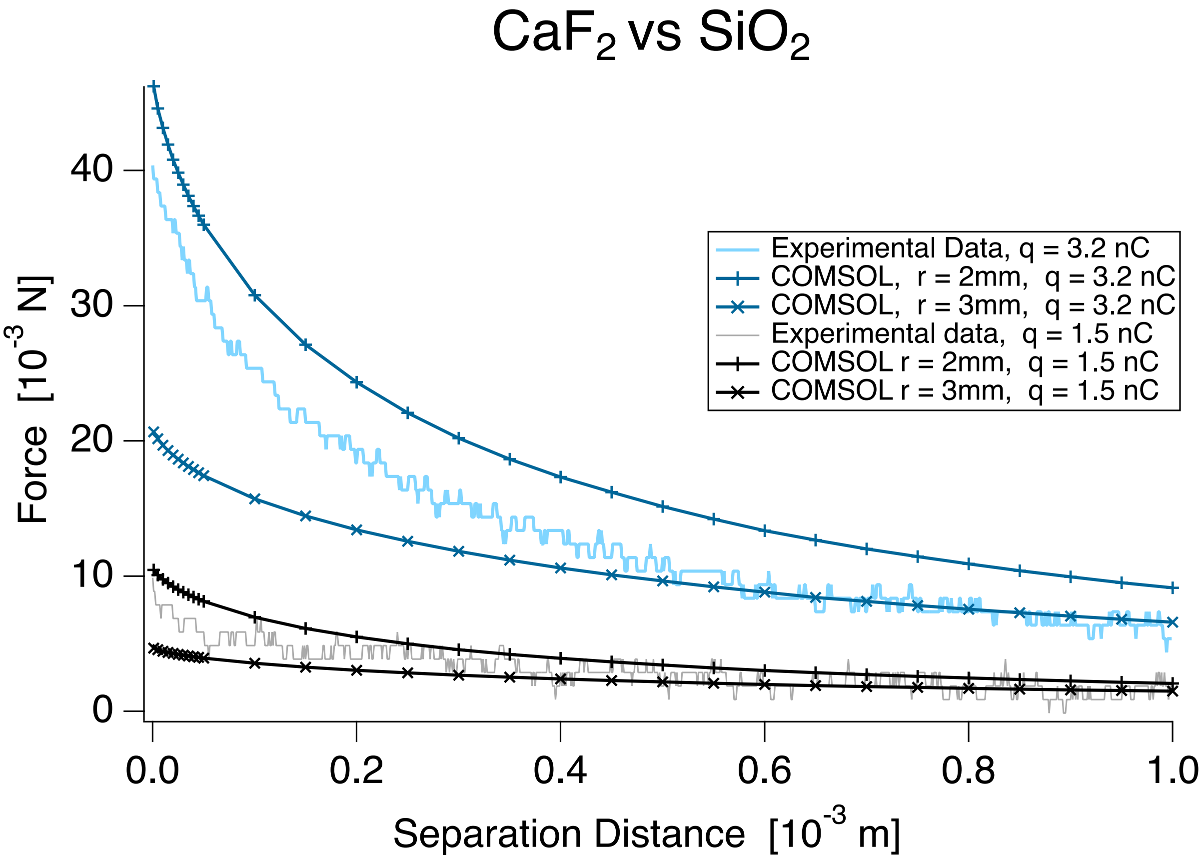

Figure 7.6: Depicted here are the force versus separation curves for two contacts within a single run of CaF_2 contacting SiO_2. The force curve with a larger magnitude occurs during a later contact when the net charge on the crystals is $3.2nC$ compared to the lower curve which occurs at an earlier contact when the net charge was $1.5nC$. The experimental data is complemented with two COMSOL simulations for a single polarity patch with the corresponding net charge, for both a radius of $2mm$ and $3mm$.

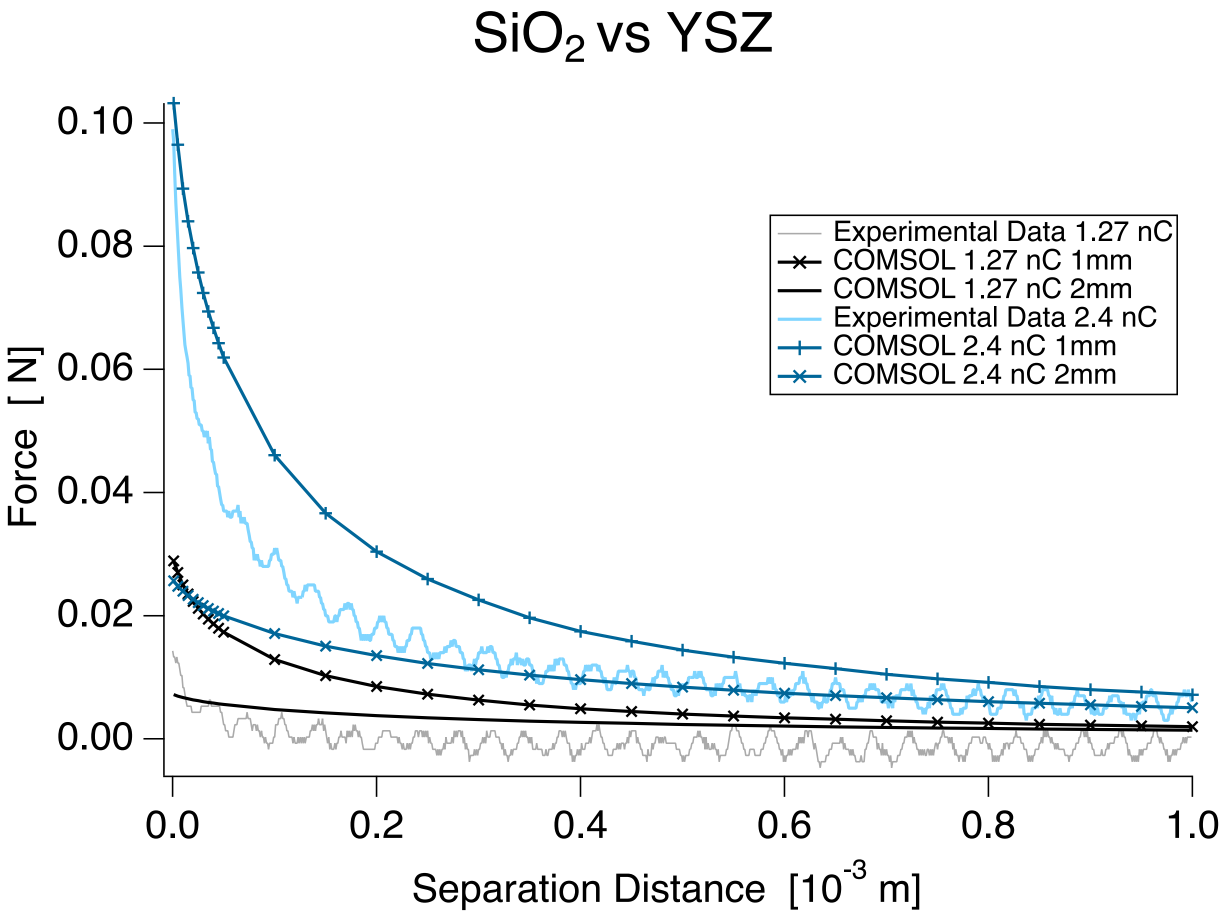

Figure 7.7: Depicted here are the force versus separation curves for two contacts within a single run of SiO_2 contacting YSZ. The force curve with a larger magnitude occurs during a later contact when the net charge on the crystals is $2.4nC$ compared to the lower curve which occurs at an earlier contact when the net charge was $1.27nC$. The experimental data is complemented with two COMSOL simulations for a single polarity patch with the corresponding net charge, for both a radius of $1mm$ and $2mm$.

7.3 Discussion

Our results for self-charging between two samples of the same single-crystal material are significant both because they identify a possible key reason contact electrification experiments tend to be so hard to reproduce and thus why it has proven so difficult to develop any widely accepted quantitative theory of the phenomenon, and because they provide evidence of our force probe's method to identify details of the charge distribution on materials after contact electrification, which in turn could lend critical insight to the mechanism behind the observe charge transfer. Our experiments between dissimilar materials were designed to make the minimize the variations in charging behavior from run to run by using smooth single-crystals to reduce bulk and surface differences from one location to the next, running experiments in vacuum at pressures to minimize variations due to sporadic discharges, choosing materials that could minimize reactivity or material transfer, using flat materials in an attempt to maximize symmetry and increase odds of similar contacts and contact areas from run to run, and rubbing to minimize the effect on charging behavior of slightly changing the contact position from run to run which could be significant depending on the details of the surface asperities on individual crystal samples. Despite this significant, though not exhaustive, effort to maximize repeatability between runs we observe not only large variations in charge transfer magnitude between dissimilar materials, but even polarity flips between runs for multiple crystal pairs, as seen in Figure 1.4. While these variations might initially be attributed to a poorly designed experiment where the quality of contact varies substantially from run to run, severely impacting the magnitude of charging, and the polarity flips are rare enough it is tempting to attribute them to some foreign contaminate on the surface and is the material that is actually being charged and thus arguing that data should simply be thrown out as an outlier, our self-charging data hints at a completely different explanation that has profound impacts on potential interpretations of contact charging experiments. The large variation in self-charging for CaF_2 and YSZ and the large magnitude of self-charging for SiO_2 and YSZ which are comparable to the largest magnitudes of charge transfer in our experiments between dissimilar materials indicates that there is some mechanism that can drive charge transfer between samples of the same crystal material at the same magnitude as the mechanism between dissimilar materials. This mechanism could be unique to interactions between the same type of crystal material, but if it is not then it must be taken into account when interpreting results of charge transfer between dissimilar materials as well. If this mechanism is universal then understanding how to control or account for its effect is critical to understanding and isolating the mechanism that appears to cause certain materials to charge with a given polarity and possibly magnitudes relative to others. It could be that when the self-charging mechanism is removed as a factor, the remaining charge transfer is robust and repeatable, lending itself to more easily described by theory.

The self-charging experiment also provides key data to test and confirm the reliability of our force probe method for determining the charge distribution on the crystal surfaces after charge exchange. Bipolar charging has been observed between dissimilar polymers, as discussed in the key experiments section, but this occurred in when the net charge transfer was small relative to our experiments. The fact that our charge transfer can be an order of magnitude larger and that we use smooth single-crystals instead of polymers provides reason to doubt that our pairs of different crystals exhibit this same bipolar charging phenomenon. However, in our experiments using two samples of the same crystal material there is no reason that one crystal should be inclined to transfer charge of a given polarity to the other, and thus it is reasonable to expect that in these experiments the observed net charge is due to pseudo-random bipolar charging, where some small asymmetry leads to a net charge, though this is not guaranteed. Further reason to expect bipolar charging is the observation that for our self-charging experiments there are polarity reversals for multiple crystal types, suggesting that the charging polarity is not determined by some constant asymmetry. This then suggests that we can compare our force measurements between the self-charging experiments and the experiments between different crystal materials and check that the self-charging pairs exhibit force profiles similar to our COMSOL simulations of bipolar charging with a net charge in one direction, and that the experiments between dissimilar materials exhibit force profiles more similar to our simulations with no or substantially reduced bipolar charging. Indeed it can be seen that for Al_2O_3 contacting SiO_2 the single polarity COMSOL simulations are reasonably close to our experimental data, to the point where a small change in the

Our data from our force measurements is highly significant with regards to future experimentation and probing techniques. It is worth noting that unlike an AFM used as a Kelvin probe where data acquisition is limited by the speed you can reliably oscillate a probe tip and capture force data from its interaction and then move the tip to the next spot on the surface to be sampled and repeat the procedure, for which the settling time for the voltage reading to become stable can limit the scan rate to $\sim$10 -100ms/pixel [83, 84], our bulk force measurement as a function of distance is only limited by the sample rate of the load cell. Further, while KPFM has been able to resolve atomic-scale features, these experiments have required UHV and sometimes cryogenic temperatures, only cover scan several nanometers in radius, require samples only a few molecular levels thick or even single molecules, and do not provide fully reliable magnitude readings due to charge polarization interactions between the tip and sample surface [25, 26, 27]. In experiments with contact electrification where these conditions cannot be met due to requirements of thicker samples, larger scan areas, or conditions other than UHV in order to contact materials, spacial resolution is limited substantially, with geometric factors leading to spacial resolution on the scale of the AFM cantilever width (often several tens of microns) for AM-KPFM (amplitude modulated), and a highly tip-height dependent resolution for FM-KPFM (frequency modulated) which can reach 10 nm resolution at a tip height of 5 nm, but falling to 200 nm at a tip height of 50 nm [85]. Thus, the KPFM's largest advantage, it's resolution, is largely negated in contact electrification where bringing a metal tip close to the charged surface can influence the charge distribution, and measuring at any significant dramatically compromises the resolution. The new probing technique presented here is superior not only in ability to measure charge distributions in a non-interfering manner *in-situ* in larger areas at higher speeds, but if the resolution is taken to be on the order of the actuator's resolution (in our case $\sim$ 30 nm) in determining separation distance, then it is possible for this method to even achieve better resolution than a KPFM scanning at a 50 nm height. This allows knowledge of the surface charge distribution to be acquired more precisely and faster than with previous techniques while having the additional advantages of collecting data in real time while avoiding any interference at the interface between the materials, providing a pathway to investigate contact electrification in unprecedented detail and perhaps even revealing fine details necessary to finally develop a comprehensive theory of the phenomenon.

7.4 Future Experiments

In addition to general experiments designed to address the remaining questions outlined in the Parameters of Investigation section that we were not able to address in our experiments, we will outline here future experiments that we believe would be the most enlightening and that would enable a rapid development of a complete theory of contact electrification.

Wang, Satio, Chen, Mastubara, Ueno, Kawasaki, and Ikuhara provide a detailed analysis of the atomic structure in the region between $CuScO_2$ and $MgAl_2O_4$ crystals [39]. In this paper the authors use transmission electron microscopy to image the interface and utilize a high-angle annular dark-field imaging mode to locate individual atoms in the interface. They are able to show that at the interface between the $CuScO_2$ and $MgAl_2O_4$ bulk materials there is a monolayer formed with different structure and chemistry than any single layer in either of the bulk materials. for their work the crystals are grown one on top of the other from the beginning, but if this imaging technique could be applied to two crystals that are prepared separately and then brought into contact the information on the structure and chemistry at the interface of the materials could provide valuable information on how any reconstruction that takes place upon contact could contribute to charge exchange.

Experiments into whether the mechanism behind contact charging can be depleted or not could also provide valuable insight as to what the charge carriers in contact electrification are. In any contact electrification experiment the charge will eventually plateau due to discharge between the two materials involved. However, it is not clear whether the plateau is only due to this effect or whether the underlying mechanism behind contact electrification can actually be depleted. Further, if the mechanism is able to be depleted, it is important to understand whether or not it can be replenished, for example by a surface treatment such as cleaning or electron bombardment. With a fully automated experiment, such as the one described in our experimental section, should be able to run indefinitely to an arbitrary large number of contacts. In such a case the investigator can simply run the experiment as long as there are still occasional discharges and then integrate the total transferred charge (that is only add charge transfer that has the polarity of primary charging, and ignore discharging events). If this can be run for long enough periods then one should be able to determine if the charge transfer can occur a larger magnitude than that which would be given by the transfer of a fundamental charge carrier at every lattice point (or a small multiple of such, if ion transfer is expected and the ions can be doubly ionized or more). Then if there is no depletion of the charge mechanism at such a key value, when ion transfer would suggest the surface of the ion-receiving material should be completely saturated, then this could be critical evidence as electrons as the charge carrier. This could be further substantiated by expanding on the work of A.L. Collins [6], and carefully monitoring x-ray emissions concurrent with discharge event. If the detector is well calibrated the exact portion of discharge due electrons as evidence from their braking-radiation spectrum should help to know exactly when a mechanism that relies on ion based charge carriers should be fatigued. We performed preliminary experiments investigating any depletion in the charging mechanism, an example of such an extended experiment is shown in Figure 7.8 over the course of 4,000 contacts. In this experiment an integrated charge transfer of $162 \cdot 10^{-}9\ C$ is reached and there is no clear indication the charging mechanism is being fatigued. Future experiments with higher integrated charge transfer (to the key values mentioned above) should shed light on the nature of the charging mechanism.

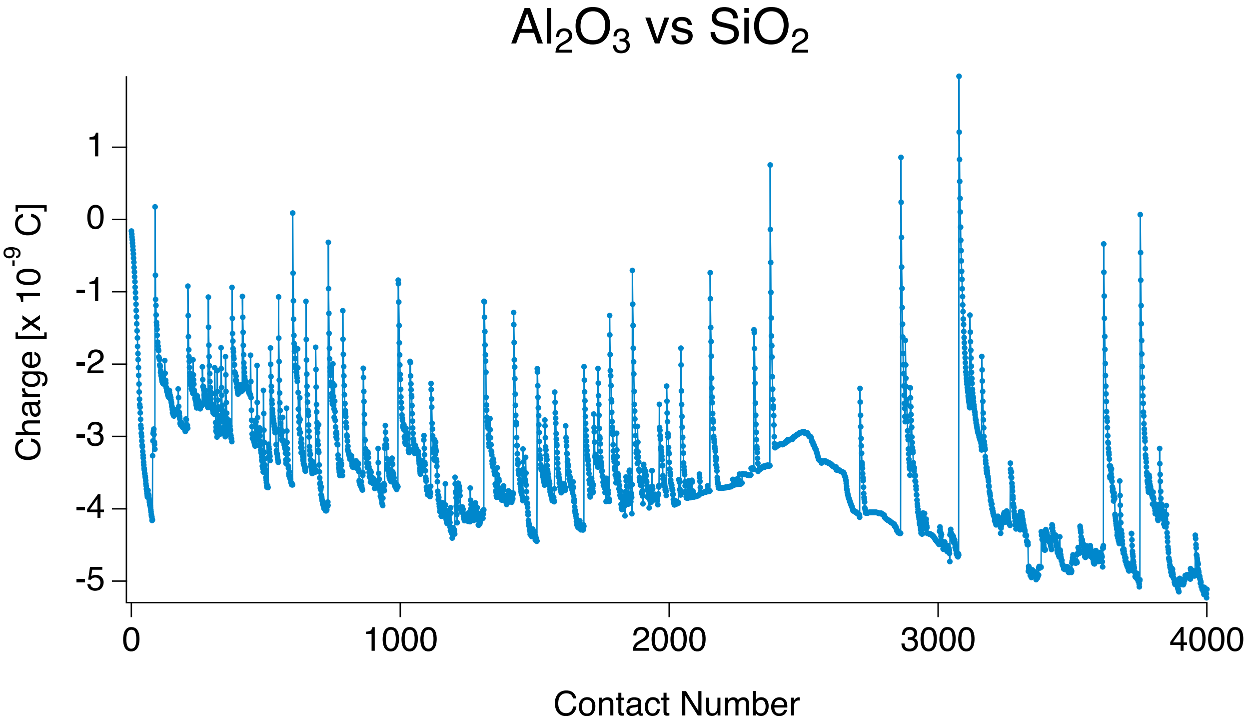

Figure 7.8: Preliminary results for an extended charging experiment to investigate crystal fatigue. In this individual run the integrated charge transferred (not subtracting discharge) is $162{\cdot}10^{-9}\ C$ over the course of 4,000 contacts, and the crystals do not display any indication of the charge transfer mechanism becoming saturated.

While our results on self-charging of single-crystals constructed of the same material puts constraints on theories attempting to explain contact electrification, a more controlled version of the same experiment could provide invaluable clues to the fundamental mechanism underlying contact electrification. In our experiments the crystal surfaces are not carefully controlled for, and the experiments are run in only a moderate vacuum, and the chamber is in a standard laboratory as opposed to a high grade clean room. If the crystals were to be cleaved *in-situ* in a ultra-high vacuum chamber located in a clean room and their surfaces characterized before contact electrification and between each contact as charge accumulates, then a much more detailed understanding of the mechanism behind self-charging could be attained. In such a situation it would prove much easier to determine the influence of surface reconstruction as opposed to the influence of surface contaminants, and any variations in surface conditions could be well correlated to charge distribution using a mechanism such as an expansion of our force-probe technique as outlined in the discussion section. Additionally, such an experiment could put strict limits on the relative contribution of the bulk material compared to surface effects, which in turn would lay the ground work for developing a complete theory of contact electrification.

Theories of contact electrification that argue for electrons as the charge carrier could rely on arguments regarding electron energy levels in the two interacting materials, and vacant versus occupied states. In such theories if the difference in energy levels is sufficient placing a conducting material between the two contacting insulators should not influence the polarity of charge transfer and any difference in the magnitude of charge transfer between the insulators should be observable as charge transferred to the conductor instead. In fact if the metal has energy states with energy levels between the relevant occupied (donating) and vacant (receiving) states in their respective materials then the metal should have would have no influence on the charge transfer for energy driven mechanisms with electron charge carriers if the number of receiving and donating states are equal, as the metal energy levels might initially start out close to one material than the other, but as it donates electrons it will now have a new open receiving state for each donated electron and the other material will now be able to donate the same number of electrons to the metal as the metal donated, leaving no net change in charge transfer. If instead the number of donating and receiving states are different, then a metal with energy states in between the energies of these states will separately deplete and fill these states, respectively, leaving a net charge on the metal equal to the charge of an electron multiplied by the difference in number of states. If this were the case there would be a second indication of such a mechanism- there would be a phenomenon where since the crystal with fewer states determines the magnitude of charge transfer, one would observe this crystal to have the same magnitude of charge transfer when contacted with any material that has a larger number of states. Then any of these crystals with a large number of states would display the same phenomenon when contacting other materials with even greater number of states. This would lead to observation of materials following a "triboelectric series" in terms of polarity, such that a material higher on the list will always charge positively relative to a material lower on the list, but there would be no correlation between position in the series and magnitude of charge transfer. That is, two materials further apart on the list than another pair will not transfer more charge to each other, instead for any given material one would observe the same charge transfer for when the other material has a greater number of receiving or donating states, as appropriate for the relative position in the series, and then would have a unique transfer when contacted with each material with a fewer number of states. Thus, for a "triboelectric series" with 20 materials it would be likely, for example, that the bottom material would have a charging pattern where 9 of the other materials transfer the exact same charge to it (and those materials would not be next to each other in the series) and then 10 of the materials would have completely unique magnitudes of charge transfer. This property would be transitive such that if material A has fewer states and is lower in the series than B, and B has fewer states and is lower in the series than C, and D, then B would have the same magnitude of transfer for C and D and A would have the same transfer for B, C, and D. If instead of a material having the vast majority of available donor or receptor states at a single energy level, the material had some distribution of states versus energy level then the magnitude of charge would not have such a simple dependence on the material with fewer available states. However, a clever investigator could then piece together the rough distribution of states by collecting data on a sufficiently large set of materials. Further, if the number of donor states per energy could probed via a photoelectric effect analogue in insulators then robust predictions of charge transfer magnitude should be achievable. Such an experiment should be clear constraints on whether ions can be the charge carrier at all, and if charge transfer is not substantially altered should be able to place limits on the mechanism that would drive electron charge carriers.

Another experiment that would lend insight into the underlying mechanism behind contact electrification, independent of charge carrier, is to carry out the experiment in the presence of a controlled electric field. If electrodes are placed behind the contacting insulators in the experiment and a potential is applied between them, then the change in electric field between the insulators can be calculated. If the driving force behind the charge transfer is an electric field created by differences in crystal potential, analogues of Fermi level, or double layer effects then the changing electric field should be able to modify magnitude of charge transfer, and at high enough fields even reverse polarity. If there is no change in charging behavior when an external electric field is applied, it would indicate the mechanism behind transfer must either be mechanical (material transfer) or chemical (individual molecular reactions, similar to those in a battery) in nature. The thought behind the experiment is simple in nature, but careful control must be exercised to avoid accidental charge transfer from the electrodes to the contacting materials, to prevent ions or electrons in the ambient environment being driven towards one material or the other, simulating contact charging, and to prevent unaccounted for discharges which could be misinterpreted as a change in the actual charging behavior.

Further, building on our observations of self-charging, and the possible nucleation mechanism discussed above, a key experiment would be to investigate whether intentionally placing seed charges can change the polarity of contact charging, both for self-charging and for pairs of dissimilar materials. This is related to an experiment where a relative voltage is applied between the materials, but is fundamentally different and might be more relevant for the insulators we are focused on. In general, the novel probe presented in this thesis which enables *in-situ*, non-invasive measurements while capable of monitoring the evolution of the charge distribution on contacting insulators from one contact to the next allows for information on the underlying mechanism behind contact electrification to be extracted for a wide range of experiments in an unprecedented way.

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